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Sulfur and lead isotopic compositions of massive sulfides from deep-sea hydrothermal systems: Implications for ore genesis and fluid circulation

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ABSTRACT

Studies of sulfur and lead isotopic compositions in hydrothermal deposits are an important tool to determine the source and processes of both sulfur and lead, and to understand the origin of hydrothermal ore deposits. Here, the sulfur and lead isotopic compositions of sulfide minerals have been studied for different hydrothermal fields in the East Pacific Rise (EPR), Mid-Atlantic Ridge (MAR), Central Indian Ridge (CIR), Southwest Indian Ridge (SWIR), and North Fiji Basin (NFB). The sulfur isotopic compositions of the studied sulfide samples are variable ($\delta^{34}\text{S}$ 0.0 to 9.6‰, avg. $\delta^{34}\text{S}$ 4.7‰; $n = 60$), being close to the associated igneous rocks ($\sim 0\text{‰}$ for, e.g., basalt, serpentized peridotite), which may reflect the S in the sulfide samples is derived mainly from the associated igneous rocks, and a relatively small proportion ($<36\%$) of seawater sulfur incorporated into these sulfides during mixing between seawater ($\delta^{34}\text{S}$ 21‰) and hydrothermal fluid. In contrast for a mixed origin for the source of S, the majority of the lead isotopic compositions ($^{206}\text{Pb}/^{204}\text{Pb}$ 17.541 ± 0.004 to 19.268 ± 0.001 , $^{207}\text{Pb}/^{204}\text{Pb}$ 15.451 ± 0.001 to 15.684 ± 0.001 , $^{208}\text{Pb}/^{204}\text{Pb}$ 37.557 ± 0.008 to 38.988 ± 0.002 , $n = 21$) of the sulfides possess a basaltic Pb isotopic composition, suggesting that the lead in the massive sulfide is mainly leached from local basaltic rocks that host the sub-seafloor hydrothermal systems in sediment-free mid-ocean ridges and mature back-arc basins. Furthermore, sulfide minerals in the super-fast and fast spreading mid-ocean ridges (MORs) exhibit less spread in their the $\delta^{34}\text{S}$ values compared to sulfides from super-slow, and slow spreading MORs, which

is most easily explained as a lesser degree of fluid-rock interaction and hydrothermal fluid-seawater mixing during hydrothermal ore-forming process. Additionally, the S and Pb isotope compositions of sulfides are controlled by the fluid processes for forming seafloor massive sulfide deposits. We demonstrate that the variable sulfur and lead isotopic compositions exhibit a relationship with the sulfur and lead sources, fluid-rock interaction, and fluid-seawater mixing.

Keywords: Sulfur and lead isotopic compositions; Massive sulfides; Seafloor hydrothermal systems

1. Introduction

Sulfur (S) and lead (Pb) isotopes are powerful tracers for exploring seafloor hydrothermal processes, fluid-rock interaction, and magmatic activity, in order to interpret the origin of hydrothermal ore deposits, in particular the sources of S and Pb in sulfide minerals (e.g., Shanks and Niemitz, 1982; Fouquet and Marcoux, 1995; Ohmoto and Goldhaber, 1997; Bjerkgaard et al., 2000; Hannington et al., 2005; Kim et al., 2006; Seal, 2006; Yao et al., 2009; Zeng et al., 2010; Aoyama et al., 2014; McDermott et al., 2015). The S and Pb isotope characteristics of massive sulfide deposits from modern seafloor hydrothermal systems in mid-ocean ridges (MORs) and back-arc basins (BABs) have been summarized by Halbach et al. (1989, 1997), Fouquet and Marcoux (1995), Verati et al. (1999), Seal et al. (2000), Zeng et al. (2000a, b), Shanks (2001), Cousens et al. (2002), Kim et al. (2004, 2006), Hannington et al. (2005), and Yao et al. (2009).

Sulfur isotopic values of seafloor hydrothermal sulfides indicate that the sulfur is most likely derived from multiple sources: (1) seawater sulfate ($\delta^{34}\text{S} \sim 21\text{‰}$); (2) igneous-rock-derived sulfur ($\delta^{34}\text{S} \sim 0\text{‰}$), including mid-ocean ridge basalt, mantle peridotites, and calc-alkaline volcanic rocks (e.g., andesites, rhyolites); (3) magmatic sulfur derived from magmatic degassing (e.g., $\delta^{34}\text{S} -5\text{‰}$ of sulfides from the Hine Hina field in the Lau basin; Herzig et al., 1998a); and (4) bacteriogenic sulfide from sediments (e.g., Ohmoto and Rye, 1979; Shanks et al., 1981, 1995; Shanks and Niemitz, 1982; Solomon et al., 1988; Peter and Shanks, 1992; Herzig et al., 1998a). For sediment-

starved MORs, the variation in the sulfur isotopic composition of the sulfides is explained by varying proportions of reduced seawater sulfate and mantle-derived sulfur leached from the underlying igneous rocks (e.g., Arnold and Sheppard, 1981; Herzig et al., 1998a). In contrast, for sediment-associated MORs, negative sulfur isotope values generally occur along with low sulfide-sulfur contents and can be caused by bacterial sulfate reduction (Goldhaber and Kaplan, 1980; Brunner and Bernasconi, 2005). Furthermore, because the equilibrium fractionation between H_2S and sulfides is limited at temperature $\geq 250^\circ\text{C}$, variation in the $\delta^{34}\text{S}$ values of sulfides can be interpreted as temporal variations in the $\delta^{34}\text{S}$ values of H_2S in the hydrothermal fluids (Styrt et al., 1981; Bluth and Ohmoto, 1988). However, the variation in the $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values could have been caused by the variation in $\delta^{34}\text{S}_{\text{ZS}}$, the pH and redox state (i.e., $\text{SO}_4^{2-}/\text{H}_2\text{S}$ ratio), or by the degree of sulfur isotopic equilibrium between SO_4^{2-} species and H_2S species in the fluid (Ohmoto and Rye, 1979). It is also unlikely that kinetic isotopic effects played an important role in the variation of $\delta^{34}\text{S}$ values of vent fluids and hydrothermal sulfides (Bluth and Ohmoto, 1988). Therefore, the variation in sulfur isotopic compositions of hydrothermal sulfides might be due to changes in the end-member fluid composition, *in-situ* sulfate reduction, or local disequilibrium sulfur isotopic fractionation during sulfide deposition (Fouquet et al., 1996). In addition, the $\delta^{34}\text{S}$ values of sulfides essentially reflect the isotope fractionation factor between sulfate (SO_4) and sulfide (H_2S) (Ohmoto et al., 1983; Ohmoto and Goldhaber, 1997), and the isotope fractionation factors between SO_4 and H_2S are 21‰ and 15‰ at 300 and 400 °C, respectively (Ohmoto and Lasaga, 1982).

For the sulfur isotope system, Farquhar et al. (2003) and Johnston et al. (2005a) demonstrated that bacterial sulfate reduction follows a mass-dependent relationship that is measurably different (i.e., $^{33}\alpha = ^{34}\alpha^{0.512}$) from that expected from thermochemical equilibrium (i.e., $^{33}\alpha = ^{34}\alpha^{0.515}$). As a result, natural samples can show measurable and systematic variations in $\Delta^{33}\text{S}$ ($=\delta^{33}\text{S}-0.515 \times \delta^{34}\text{S}$) as well as $\Delta^{36}\text{S}$ ($=\delta^{36}\text{S}-1.90 \times \delta^{34}\text{S}$) even when $\delta^{34}\text{S}$ values are identical (Ono et al., 2006). In the Lau basin, isotopically light sulfur ($\delta^{34}\text{S}$ -5‰), which is observed in the sulfides from the Hine Hina field, may be produced in several ways, including biogenic reduction of seawater SO_4 , fractionation of sulfur between reduced and oxidized species as a result of large shifts in the oxidation state of the fluids (e.g., by boiling), or by the evolution of light sulfur directly from a magmatic volatile phase (Herzig et al., 1998a).

Furthermore, in the Trans-Atlantic Geotraverse (TAG) hydrothermal field, the range of sulfur isotopic compositions of sulfides is significantly larger (4.4 to 8.9‰) than that of sulfides from the EPR near 21°N and 13°N, which has been interpreted to suggest that the TAG hydrothermal massive sulfides formed as a result of multiple-stages of hydrothermal activity (Stepanova et al., 1996; Knott et al., 1998). In addition, on the EPR near 21°N, the $\delta^{34}\text{S}$ values of the late-stage pyrite samples, which appear to infill fluid conduits, are among the lowest observed, suggesting precipitation in the fluid conduits of sulfide deposits isolated from seawater influx or perhaps at temperatures below 200–250°C, above which sulfate reduction becomes rapid (Shanks et al., 1981; Ohmoto and Lasaga, 1982; Woodruff and Shanks, 1988).

Lead isotopic compositions of seafloor hydrothermal sulfides indicate that the lead is

most likely derived from three sources: (1) basalts at MORs (e.g., Brévar et al., 1981; LeHuray et al., 1988; Fouquet and Marcoux, 1995; Zeng et al., 2010); (2) sediments at BABs (e.g., Halbach et al., 1997; Zeng et al., 2000b) and MORs (e.g., LeHuray et al., 1988; Zierenberg et al., 1993; Cousens et al., 2002); (3) volcanic rocks that have inherited lead from the subducted slab, including basalt and its sediment at BABs (Fouquet and Marcoux, 1995; Kim et al., 2004). On sediment-starved ridges, the Pb in hydrothermal sulfides is considered to have been mobilized from the volcanic crust during hydrothermal circulation based on the sulfide Pb isotope compositions that are indistinguishable from that of the local basalt (e.g., Brévar et al., 1981; Vidal and Clauer, 1981; LeHuray et al., 1988; Fouquet and Marcoux, 1995; Andrieu et al., 1998; Zeng et al., 2010). The Pb isotopic compositions of the sulfides are also more homogeneous than the adjacent volcanic rocks, suggesting that the Pb isotopes have been homogenized during hydrothermal circulation, and that the contribution of Pb from seawater and hemipelagic sediments is very low (e.g., Brévar et al., 1981; Vidal and Clauer, 1981; Chen, 1987; Hegner and Tatsumoto, 1987; LeHuray et al., 1988; Fouquet and Marcoux, 1995; Andrieu et al., 1998; Charlou et al., 2002; Yao et al., 2009; Zeng et al., 2010).

Furthermore, on sediment-covered MORs, such as the Middle Valley on the Juan de Fuca Ridge, the Escanaba Trough in the Gorda Ridge, and the Guaymas Basin in the Gulf of California, the Pb in the seafloor hydrothermal sulfides is considered to have been sourced from both the mid-ocean ridge basalt (MORB) and the sediment (LeHuray et al., 1988; Goodfellow and Franklin, 1993). In this setting, the sulfides

possess a larger range and more radiogenic compositions due to a contribution of lead from the pelagic and terrigenous sediments, in addition to basalt lavas, through which the hydrothermal fluids have passed (e.g., LeHuray et al., 1988; Zierenberg et al., 1993; German et al., 1995; Stuart et al., 1999; Bjerkgård et al., 2000; Cousens et al., 2002, 1995).

In contrast to the Pb isotopic compositions of sulfides from sediment-starved MORs, the Pb isotopic characteristics of seafloor hydrothermal sulfides in the Jade hydrothermal field of the Okinawa Trough are distinctly different, which can be interpreted as a mixture of roughly equal parts of volcanic lead with lead derived from the Okinawa Trough sediments (Halbach et al., 1997; Zeng et al., 2000b). The Pb of hydrothermal sulfides in the chimneys in the Eastern Manus Basin has been leached from the surrounding andesite and dacite during hydrothermal circulation, and the slightly more radiogenic Pb isotope composition of the Susu knolls sulfides compared to those from PACMANUS, indicate that the Susu knolls site is possibly affected more by an arc component than the PACMANUS site (Kim et al., 2004). In the North Fiji Basin, the Pb of hydrothermal sulfides in chimneys is from MORB, and the formation of chimneys was possibly related to E-MORB volcanism (Kim et al., 2006). In the Lau Basin, the Pb of seafloor hydrothermal sulfides is from three end-member sources: basalts from the Pacific Ocean and Indian Ocean plates, and pelagic sediments (Fouquet and Marcoux, 1995).

In this paper, we present the first results of S and Pb isotope analyses of massive sulfides from the EPR near 1–2°S, the MAR near 13°S, the CIR at Kairei

hydrothermal field (KHF), Edmond hydrothermal field (EHF) at 25°S, and the Southwest Indian Ridge (SWIR) in area A (Fig. 1). In addition, $\delta^{34}\text{S}$ and Pb isotope analyses were performed on the massive sulfides from the EPR near 13°N and 11°N, the MAR at the Logatchev hydrothermal field (LHF), and the North Fiji BAB at the Sonne 99 hydrothermal field (S99HF) (Fig. 1). The main purposes of the paper are: (1) to investigate the characteristics of the S and Pb isotope compositions of sulfides from the EPR near 1–2°S, the MAR near 13°S, the CIR at KHF, EHF, and the SWIR in area A; (2) to characterize the sources of S and Pb; and (3) to understand the effect of fluid-rock interaction, fluid–seawater mixing, magmatic activity, and spreading rate of MORs on the S and Pb isotopic compositions of massive sulfides.

2. Geological setting and sample mineralogy

Seafloor hydrothermal sulfide samples were recovered by TV-grab samplers from the fast-spreading EPR near 13°N, the ultra-fast spreading EPR near 1–2°S, the Kairei hydrothermal field (KHF), the Edmond hydrothermal field (EHF) on the intermediate-spreading CIR near 25°S, the slow-spreading MAR near 13°S, the LHF (15°N), the ultra-slow spreading SWIR near 63.5°E and in area A (49°E) in 2005, 2007, 2008, 2009, and 2010 during the DY105-17, DY115-19, DY115-20, and DY115-21 cruises of R/V Dayang Yihao. Sulfide samples from the Sonne 99 hydrothermal field (S99HF) in the back-arc North Fiji Basin (NFB) were collected in 1998 during the SO134 cruise of HYFIFLUX II (Fig. 1).

At the EPR near 13°N, 11°N, and 1–2°S, the KHF, EHF, the MAR near 13°S, the area A, and the S99HF, the seafloor hydrothermal sulfides are hosted by mid-ocean ridge basalts (MORBs) (e.g., Kumagai et al., 2008; Zeng et al., 2010, 2014, 2015a, b). The KHF is situated on basaltic rocks, but the hydrothermal fluids also interact with and circulate through ultramafic rocks (Nakamura et al., 2009). In the LHF, the hydrothermal sulfide deposit is associated with ultramafic rocks located in a debris flow consisting of heterogeneous ultramafic and mafic intrusive rocks, including serpentized harzburgite, serpentized dunite, gabbro-norite, and olivine-bearing basalt (e.g., Petersen et al., 2009; Zeng et al., 2014, 2015a, b). In addition, in the North Fiji Basin, the S99HF is located immediately south of the triple junction point at 16°50'S and is hosted by basaltic rocks, the trace element composition of which indicates that magma generation was influenced by two different sources: normal mid-ocean ridge basalt (N-MORB) and ocean island basalt (OIB)-related to enriched mid-ocean ridge basalt (E-MORB) (Eissen et al., 1994; Nohara et al., 1994; Koschinsky et al., 2002; Kim et al., 2006).

3. Samples and analytical methods

3.1. Sampling procedures

Table 1 and Figure 1 show the sampling location, depth, and mineralogy of the hydrothermal sulfide samples. Seafloor hydrothermal sulfide samples consist of major pyrite ± marcasite, chalcopyrite, sphalerite, anhydrite, barite, and amorphous silica.

Sulfide mineral aggregate samples were taken from different seafloor hydrothermal sulfide deposits. Samples denoted as pyrite, sphalerite, and chalcopyrite + pyrite consist of abundant (>30%) pyrite, sphalerite, and chalcopyrite + pyrite, respectively. All samples for S and Pb isotope analysis were crushed and sieved to select sulfide aggregates between >1 mm and 1 cm. All sample chips were crushed with an agate mortar and pestle and sieved to select sulfide grains between 50 μm and 2 mm in size (Zeng et al., 2014, 2015a, b). The sulfides were separated from non-sulfide minerals, e.g., sulfates and amorphous silica, via ethanol elutriation (Zeng et al., 2014, 2015a, b). This purification of the sulfide aliquots by ethanol elutriation is based on specific gravity and uses a stream of ethanol that flows counter to the direction of grain flow in a glass dish. The less dense particles rise to the top (overflow) because their terminal grain velocities are lower than the velocity of the rising fluid. Because most of the samples were fine-grained and intergrown, an integrated mechanical separating method was used to obtain a monomineralic sulfide or mineral aggregate. The separation methods included a high-frequency dielectric splitter, magnetic separator, and electromagnetic separator (Zeng et al., 2014, 2015a, b). All sulfide samples were then carefully picked manually under a binocular microscope to avoid sulfates and oxides, and were ultrasonically cleaned in ultrapure alcohol to remove any seawater influences, e.g., the presence of salts and altered seawater products. Then, all the samples were ground to a powder finer than 63 μm in an agate mortar (Zeng et al., 2014, 2015a, b). Fine-grained glass powder was used as an abrasive to polish the mortar and pestle between samples to exclude cross- contamination. In addition, one

sulfate sample was also prepared by hand picking and was similarly prepared for sulfur isotopic analysis.

3.2. Analytical methods

Sulfide samples (<0.1 mg) were combusted in a tin cup using a modified Roboprep elemental analyzer attached to a Finnigan 252 mass spectrometer at the Environmental Isotopes Pty Ltd., Macquarie Center, NSW 2113, Australia. V_2O_5 was added to the sulfate samples and standards to enhance combustion. Samples were analyzed relative to an internal gas standard and laboratory standards (Ag_2S -3, $\delta^{34}S = +0.4\text{‰}$ VCDT and CSIRO-S- SO_4 , $\delta^{34}S = +20.4\text{‰}$ VCDT). The laboratory standards had been calibrated using international standards IAEA-S1 ($\delta^{34}S = -0.3\text{‰}$ VCDT) and NBS-127 ($\delta^{34}S = +20.3\text{‰}$ VCDT). Replicate analyses of sulfide standards were within $\pm 0.2\text{‰}$.

Lead abundances were measured on separate 40-mg splits of powdered sulfide aggregates. These pretreated samples were digested in vials by using 0.5 mL of 22.5 mol/L HF, 2 mL of 12 mol/L HCl and 0.7 mL of 16 mol/L HNO_3 (all acids at metal-oxide-semiconductor pure grade) at 150°C for 24 h in closed Teflon vials on an electrothermal hotplate. Then, 0.2 mL of 12.4 mol/L $HClO_4$ was added, and the samples were dried at 120°C until no white smoke was present. When the samples were almost dry, 1 mL of 16 mol/L HNO_3 and 1 mL of deionized Milli-Q water (18.2 M Ω cm resistivity) were added, and the mixture was re-heated in closed vials on the hotplate at 120°C for 12 h (Yin et al., 2011). Finally, Pb was analyzed by an IRIS

Intrepid II XSP ICP-AES (Thermoelectricity Company) at the Qingdao Institute of Marine Geology. The reference materials GBW07267, GBW07268, GBW07270, and WMS-1A were run as external standards to evaluate the accuracy. The relative standard deviation (RSD), which was calculated from standard reference materials, was <2%.

Between 100 and 200 mg of powdered sulfide aggregates were dissolved in 50% HF-12N HNO₃, then treated with 8N HNO₃ and finally 6N HCl. The residue was taken up in 1N HBr, and Pb was separated on Bio-Rad 10-ml polyethylene columns and Dowex AG1-8X anion resin, using 6N HCl to elute Pb. The collected Pb solution was dried and redissolved in 1N HBr, and the above procedure was repeated with a small-volume resin bed. Samples were loaded onto single Re filaments with H₃PO₄ and silica gel and were analyzed at the Department of Earth Sciences, Carleton University, with a Triton Tl thermal ionization mass spectrometer. Total procedural blanks for Pb were <450 pg. The average ratios measured for NBS 981 were $^{206}\text{Pb}/^{204}\text{Pb} = 16.888 \pm 0.007$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.425 \pm 0.009$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.492 \pm 0.030$. One duplicate run of sample 19III-S12-TVG6 showed good agreement between the two results (Table 4).

4. Results

4.1. Sulfur isotopic compositions in sulfides

Sulfide minerals forming in the EPR near 13°N, 11°N, and 1–2°S, the LHF, the MAR

near 13°S, the KHF, the EHF, the CIR near 25°S, area A, and the S99HF exhibit a range of $\delta^{34}\text{S}$ values from 0.0 to 9.6‰ (see Table 2; Fig. 2), with an average value of 4.7‰ ($n = 60$), falling within the overall range of $\delta^{34}\text{S}$ values for sulfide samples from other seafloor hydrothermal field (from 1 to 9‰; $n = 1841$) (Fig. 3). A single value of 21.5‰ for the sulfate sample at the EHF falls within the overall range of sulfate samples from other seafloor hydrothermal fields (from 19 to 25‰; $n = 288$) (data are from Shanks and Niemitz, 1982; Kerridge et al., 1983; Zierenberg et al., 1984, 1993; Koski et al., 1985; Shanks and Seyfried, 1987; Hannington and Scott, 1988; Zierenberg and Shanks, 1988, 1994; Kusakabe et al., 1990; Blum and Puchelt, 1991; Iizasa et al., 1992; Peter and Shanks, 1992; Lein et al., 1993; Zierenberg, 1994; Chiba et al., 1998; Gemmell and Sharpe, 1998; Herzig et al., 1998a, b; Knott et al., 1998; Marumo and Hattori, 1999; Zeng et al., 2002a, b; de Ronde et al., 2003; Kim et al., 2004; and Rouxel et al., 2004a). Sulfide minerals from the EPR near 1–2°S have much higher sulfur isotope ratios (pyrite $\delta^{34}\text{S}$ values from 3.0 to 5.8‰, avg. 4.4‰, $n = 9$; chalcopyrite $\delta^{34}\text{S}$ values from 3.8 to 3.9‰, $n = 2$) than in the EPR near 13°N and 11°N (pyrite $\delta^{34}\text{S}$ values from 1.4 to 2.2‰, avg. 1.9‰, $n = 7$) (Fig. 2A). These values are within the range of previously reported analyses of hydrothermal sulfides from the EPR near 13°N ($\delta^{34}\text{S}$ values from 0.4 to 5.0‰, avg. 2.7‰, $n = 75$, Bluth and Ohmoto, 1988; Stuart et al., 1995; Zeng et al., 2010), 11°N ($\delta^{34}\text{S}$ values from 2.2 to 4.9‰, avg. 4.1‰, $n = 22$, Bluth and Ohmoto, 1988; McConachy, 1988), and 21°N ($\delta^{34}\text{S}$ values from 0.7 to 6.2‰, avg. 2.5‰, $n = 118$, Hekinian et al., 1980; Arnold and Sheppard, 1981; Styrer et al., 1981; Kerridge et al., 1983; Zierenberg et al., 1984; Woodruff and

Shanks, 1988; Stuart et al., 1994a) (see Table 3; Fig. 3).

In the MARs, the $\delta^{34}\text{S}$ value (4.5‰) of pyrite sample from the MAR near 13°S is significantly lower than that of chalcopyrite samples at the LHF ($\delta^{34}\text{S}$ values from 9.1 to 9.6‰) (Fig. 2B). These values are within the range of previously reported analyses of hydrothermal sulfides at the LHF (Bogdanov et al., 1997) (0.7 to 13.8‰, avg. 7.6‰, $n = 26$) but heavier than those of sulfides at the LHF reported by Petersen et al. (2005) (2.2 to 8.9‰, $n = 21$) and Rouxel et al. (2004b) (4.6 to 6.1‰, avg. 5.4‰, $n = 17$).

In the Indian Ocean, sulfide minerals at the EHF have much higher sulfur isotope ratios (pyrite $\delta^{34}\text{S}$ values from 5.2 to 7.3‰, avg. 6.3‰, $n = 8$; sphalerite $\delta^{34}\text{S}$ values from 6.1 to 7.0‰, avg. 6.4‰, $n = 7$; chalcopyrite $\delta^{34}\text{S}$ values from 6.4 to 7.5‰) than those in the KHF (pyrite $\delta^{34}\text{S}$ values from 1.8 to 2.3‰, avg. 2.1‰, $n = 3$), CIR near 25°S (chalcopyrite $\delta^{34}\text{S}$ value 5.9‰, $n = 1$), and EPR near 13°N, 11°N, and 1–2°S (Fig. 2). The $\delta^{34}\text{S}$ values (0.0 to 7.0‰, avg. 4.4‰; $n = 6$) of sulfide minerals from the area A are lower than those of sulfides from the EHF (Table 2; Fig. 2), and the majority of these values are within the range of previously reported analyses of hydrothermal sulfides from the Sonne field in the CIR (from 1.6 to 6.6‰, avg. 3.4‰, $n = 54$, Halbach and Munch, 2000).

The $\delta^{34}\text{S}$ values in sulfide minerals at S99HF vary between 2.7 and 4.0‰ (avg. 3.3‰, $n = 5$) for pyrite, 3.4 and 4.1‰ (avg. 3.7‰, $n = 4$) for sphalerite, and 4.0 and 4.2‰ (avg. 4.1‰, $n = 2$) for chalcopyrite (Fig. 1D). These values are within the range of previously reported analyses of hydrothermal sulfides from the North Fiji basin (from

0.4 to 5.6‰, avg. 3.4‰, $n = 78$, Kim et al., 2006). Furthermore, compared to the sulfur isotopic compositions of sulfides from the sediment-hosted hydrothermal fields in the Middle Valley of the northern Juan de Fuca Ridge, the Escanaba Trough of the southern Gorda Ridge, and the Guaymas Basin of the Gulf of California, the sulfur isotopic compositions of sulfide minerals from the EPR near 13°N, 11°N, and 1–2°S, LHF, MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF have a smaller range $\delta^{34}\text{S}$ values (see Table 3; Fig. 3).

In addition, if the pyrite and sphalerite had attained equilibrium at $T = 150\text{--}250\text{ }^{\circ}\text{C}$, the differences (Δ) in the $\delta^{34}\text{S}$ values should be $\Delta_{\text{pyrite-sphalerite}} = 1.9\text{--}0.8\text{‰}$, and pyrite should have a higher $\delta^{34}\text{S}$ than sphalerite (Smith et al., 1977). If the pyrite and chalcopyrite had attained equilibrium at $T = 200\text{--}400\text{ }^{\circ}\text{C}$, the differences (Δ) in the $\delta^{34}\text{S}$ values should be $\Delta_{\text{pyrite-chalcopyrite}} = 2.0\text{--}1.0\text{‰}$, and pyrite should have a higher $\delta^{34}\text{S}$ than chalcopyrite (Ohmoto and Rye, 1979). The pyrite–chalcopyrite pairs (sample 20III-S4-TVG1-2-2) from the EPR near 1–2°S, pyrite–sphalerite pairs (sample IR05-TVG12-5-2, IR05-TVG12-8-2, and IR05-TVG12-11) and sulfate–pyrite pairs (sample IR05-TVG13-9.1) from the EHF, and the pyrite–sphalerite pairs (sample 26.2GTV-1) and pyrite–chalcopyrite pairs (sample 113.1GTV-4) from the S99HF exhibit sulfur isotopic disequilibrium, based on known temperature-dependent fractionation factors, typical of most seafloor hydrothermal systems (Ohmoto, 1986). Similar sulfur isotopic disequilibrium has been identified in most investigated seafloor hydrothermal sulfide deposits (e.g., the EPR at 21°N, Arnold and Sheppard, 1981; Styr et al., 1981; Kerridge et al., 1983; Zierenberg et al., 1984; Woodruff and Shanks,

1988; the Guaymas Basin, Shanks and Niemitz, 1982; Koski et al., 1985 Peter and Shanks, 1992; the Red Sea, Shanks and Bischoff, 1977, 1980; the Axial Seamount, Hannington and Scott, 1988).

4.2. Lead isotopic compositions in sulfides

The Pb isotopic ratios of the sulfides from the EPR near 13°N, 11°N, and 1–2°S, LHF, MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF range between 17.541 ± 0.004 and 19.268 ± 0.001 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.451 ± 0.001 and 15.684 ± 0.001 for $^{207}\text{Pb}/^{204}\text{Pb}$, 37.557 ± 0.008 and 38.988 ± 0.002 for $^{208}\text{Pb}/^{204}\text{Pb}$ ($n = 21$) (Table 4).

In the EPR near 13°N, the Pb isotopic composition of sulfides from the off-axis hydrothermal field in this study are more radiogenic than that of the hydrothermal sulfides from the older off-axis seamount and the marginal high of the EPR (Fouquet and Marcoux, 1995; Zeng et al., 2010). The Pb isotopic composition of the three sulfide samples from the marginal high are closer to that of sulfide samples from the axial graben on the EPR near 13°N (Fouquet and Marcoux, 1995), with only one sample (EPR05-TVG1-3-1) possessing a more radiogenic Pb isotopic composition than sulfides from the axial graben. On the EPR near 1–2°S, three sulfide samples have similar Pb isotopic compositions, and the range of Pb isotopic compositions is narrow ($^{206}\text{Pb}/^{204}\text{Pb} = 18.156$ to 18.259 ; $^{207}\text{Pb}/^{204}\text{Pb} = 15.451$ to 15.512 ; $^{208}\text{Pb}/^{204}\text{Pb} = 37.635$ to 37.877) (Table 4), similar to that of sulfides from the EPR near 21°26'S (Fouquet and Marcoux, 1995) (see Table 5). Furthermore, the Pb isotopic composition

of the three sulfide samples from the marginal high on the EPR near 13°N was more radiogenic than that of sulfides from the EPR near 1–2°S (see Table 5; Fig. 4). In the LHF, two samples (MAR05-TVG1-10-2 and MAR05-TVG1-9) show different Pb isotope compositions (Table 4; Fig. 5). The two sulfide samples have lower $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (19.2 to 19.5) than that of sulfide samples from the Logatchev-1 hydrothermal field (Lein et al., 2001), but their $^{207}\text{Pb}/^{204}\text{Pb}$ ratios and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are similar to those of the Logatchev-1 hydrothermal field (Lein et al., 2001). In addition, the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of one sulfide sample (MAR05-TVG1-9) from the LHF are within or near the range of pelagic sediments and Fe-Mn crusts from the Atlantic Ocean, respectively (Fig. 5), and the Pb isotopic composition of this sample is also similar to the Pb isotopic compositions of the sediment-hosted sulfide deposits currently forming at the sediment-filled Escanaba Trough of the Gorda Ridge (LeHuray et al., 1988; Zierenberg et al., 1993). Sulfide samples from the LHF have Pb isotope compositions that are significantly different from those of other sulfide samples from sediment-starved ridges (such as EPR 13°N, 21°N), which have particularly low $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (Table 5). In addition, one sulfide sample from the MAR near 13°S has significantly lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than sulfide samples from the LHF (Table 4; Fig. 5). The $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is within the range of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of sulfide samples from the TAG hydrothermal field (Andrieu et al., 1998), but possesses a $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios that are significantly higher (see Table 5). Sulfide samples from the KHF and CIR near 25°S has significantly higher $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and

$^{208}\text{Pb}/^{204}\text{Pb}$ ratios than basalts from the CIR near 25°S (Table 4; Fig. 6). The majority of Pb isotopic ratios in the four samples ($^{206}\text{Pb}/^{204}\text{Pb} = 17.898$ to 17.984; $^{207}\text{Pb}/^{204}\text{Pb} = 15.453$ to 15.562; $^{208}\text{Pb}/^{204}\text{Pb} = 37.815$ to 38.173) from the EHF falls in the range of Pb isotopic composition fields of basalts from the CIR near 24°S (Table 4; Fig.6).

The range of Pb isotopic compositions of two sulfide samples in area A is narrow ($^{206}\text{Pb}/^{204}\text{Pb} = 18.149$ to 18.208; $^{207}\text{Pb}/^{204}\text{Pb} = 15.484$ to 15.491; $^{208}\text{Pb}/^{204}\text{Pb} = 37.988$ to 37.997) (Table 4; Fig. 6). In comparison to sulfides from the EHF, they possess higher $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, but similar $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (Table 4; Fig. 6). In the S99HF, the range of Pb isotopic compositions of four sulfide samples is narrow ($^{206}\text{Pb}/^{204}\text{Pb} = 18.139$ to 18.160; $^{207}\text{Pb}/^{204}\text{Pb} = 15.493$ to 15.514; $^{208}\text{Pb}/^{204}\text{Pb} = 37.960$ to 38.001) (Table 4; Fig. 7), which is within the range of the Pb isotopic composition of sulfide samples (types 2 and 3 chimneys) from the North Fiji Basin (Kim et al., 2006). In addition, sulfides from the EPR near 13°N, the EPR near 1–2°S, the LHF, the MAR near 13°S, the EHF, the KHF, area A, and the S99HF possess Pb concentrations that span a large range (1.54 to 1905 ppm), and the Pb contents of three sulfide samples from the EHF are high (1312–1905 ppm), and are independent of the Pb isotope composition (Table 4).

5. Discussion

5.1. Sulfur sources

It is known that the hydrothermal activity on the EPR near 13°N, 11°N, and 1–2°S,

MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF are hosted by mid-ocean ridge basalts (MORBs). The sulfur in basalts uniformly have $\delta^{34}\text{S}$ values very close to 0‰ ($+0.1 \pm 0.5\text{‰}$) (Sakai et al., 1984; Alt et al., 1989; Shanks et al., 1995; Alt and Shanks, 2003). Furthermore, basaltic sulfur can be efficiently leached by high-temperature (300 °C–500 °C) fluid (Mottl et al., 1979), and large sulfur isotopic fractionation does not occur during leaching, transport, or reprecipitation as sulfide minerals (Shanks and Niemitz, 1982). Seawater sulfate has a $\delta^{34}\text{S}$ value of +21‰ (Rees et al., 1978). Hydrothermal vent fluids for seafloor sulfide–sulfate mineralization typically have $\delta^{34}\text{S}$ values of H_2S that range from 1.5‰ to 7‰ (e.g., Shanks et al., 1995), which fall between the $\delta^{34}\text{S}$ values for basalts ($+0.1 \pm 0.5\text{‰}$) and seawater (+21‰). Therefore, the sulfur isotopic compositions of seafloor sulfide deposits can be used as evidence for the source of sulfur (e.g., Fouquet et al., 1996).

The $\delta^{34}\text{S}$ values of sulfide mineral samples from the EPR near 13°N, 11°N, and 1–2°S, MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF have a broad range (0.0 to 7.5‰; Table 2; Fig. 3), and are generally similar to the $\delta^{34}\text{S}$ values for hydrothermal vent fluids (1.5‰ to 7‰), which are between those of basalts and seawater (Table 2; Fig. 3).

On the MAR, the LHF is hosted by variable mixtures of serpentinized peridotite and mafic material (Delacour et al., 2008). The $\delta^{34}\text{S}$ values (9.1 to 9.6‰) of sulfide minerals at the LHF are higher than those of gabbros (-2.1 to 7.6‰; Delacour et al., 2008) from the southern wall of the Atlantis Massif. The $\delta^{34}\text{S}$ values of the sulfide minerals are also higher than those of oceanic gabbros and MORB (-2 to +2‰) (Sakai

et al., 1984; Alt et al., 1989, 2007; Alt and Anderson, 1991). The sulfur isotopic compositions of the sulfide minerals at LHF indicate contributions of sulfur from both igneous rocks and seawater sulfate. Furthermore, the $\delta^{34}\text{S}$ values of sulfide minerals at the LHF are higher than basalt-hosted hydrothermal fields (e.g., EPR near 13°N, 11°N, and 1–2°S; Table 2), and are likely to have been influenced by reduction of seawater sulfate under higher fluid fluxes, more oxidizing conditions, and sulfide leaching from serpentized peridotite and mafic material during high-temperature hydrothermal alteration (Alt et al., 2007; Delacour et al., 2008). In addition, the sulfur isotopic composition ($\delta^{34}\text{S} = 21.5\text{‰}$) of the single sulfate sample at the EHF, which is indistinguishable from that of the seawater sulfate $\delta^{34}\text{S}$ value (+21‰; Rees et al., 1978), indicates that the sulfur in sulfate is derived from seawater, which can be interpreted as evidence of entrainment of seawater into hydrothermal fluids within the chimney.

Furthermore, according to a simple two end-member mixing model ($\delta^{34}\text{S}_{\text{mix}} = X \times \delta^{34}\text{S}_{\text{seawater}} + (1 - X) \times \delta^{34}\text{S}_{\text{basalt}}$; where X is the amounts of seawater component; $\delta^{34}\text{S}_{\text{mix}}$, $\delta^{34}\text{S}_{\text{seawater}}$ (21‰), and $\delta^{34}\text{S}_{\text{basalt}}$ (0‰) are the sulfur isotopic compositions of sulfide, seawater, and basalt, respectively), the sulfur isotopic composition of sulfide minerals can be explained by disequilibrium mixing of sulfur (about 6–10%, 10%, 14–27%, 21%, 8–11%, 28%, 25–36%, 0–33%, and 12–20%) from reduced seawater sulfate with sulfur (about 90–94%, 90%, 73–86%, 79%, 89–92%, 72%, 64–75%, 67–100%, and 80–88%) of basaltic origin in the EPR near 13°N, 11°N, and 1–2°S, MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF, suggesting that the

contribution proportions of seawater sulfur are lower than that of basaltic sulfur in the hydrothermal sulfide minerals from the EPR near 13°N, 11°N, and 1–2°S, MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF.

5.2. Lead sources

The majority of Pb isotope ratios of sulfides from the EPR near 13°N and 1–2°S, MAR near 13°S, EHF, CIR near 25°S, area A, and S99HF fall in the range of Pb isotopic composition fields of basalts from the EPR, MAR, Indian ridge (IR) and North Fiji Basin (Figs. 4–7), suggesting that basalts are the principal source of lead for hydrothermal fluids (e.g., Vidal and Clauer, 1981; Chen, 1987; Hegner and Tatsumoto, 1987; Hinkley and Tatsumoto, 1987; Fouquet and Marcoux, 1995; Charlou et al., 2002; Yao et al., 2009). Furthermore, the Pb isotope data of seafloor hydrothermal sulfides define a small domain compared with the larger field of mid-ocean ridge and back-arc basin basalts. The mean Pb isotopic compositions of sulfides from the EHF, CIR near 25°S, area A, and S99HF (Table 5) are similar to that of basalts from the vicinity of the respective hydrothermal field, which suggests that the heterogeneous Pb isotope (e.g., Allègre et al., 1984; Hamelin et al., 1984) extracted from the upper oceanic crust by hydrothermal fluid are homogenized during hydrothermal circulation, supporting the conclusion of previous studies (Fouquet and Marcoux, 1995; Andrieu et al., 1998). In turn, this suggests that the average Pb isotopic composition of sulfide minerals can be used to infer the Pb isotopic composition of the local basaltic crust.

The Pb isotopic ratios of sulfides from the EPR near 13°N and 1–2°S and CIR near 25°S appear to be close to the average values of Pb isotope ratios of basalts in the EPR near 13°N and 1–2°S, and CIR near 25°S, respectively (Figs. 4 and 6), implying that seawater is not a possible source of the Pb in the sulfides. Furthermore, in the KHF, one sulfide sample (IR05-TVG-9-2) also has higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (i.e., is more radiogenic) than sulfides from the EHF and the CIR near 25°S. The Pb isotope composition plots near or within those of the Indian Ridge basaltic field, suggesting that seawater could not be a component of the source of Pb in the KHF (Fig. 6). In addition, the more radiogenic Pb isotope composition of sulfide samples from the S99HF compared to that of type 1 chimneys ($^{206}\text{Pb}/^{204}\text{Pb} = 18.082$ to 18.132 ; $^{207}\text{Pb}/^{204}\text{Pb} = 15.440$ to 15.481 ; $^{208}\text{Pb}/^{204}\text{Pb} = 37.764$ to 37.916) from the 16°53'S triple junction area in the North Fiji Basin, suggest that the Pb in the sulfides is possibly related to E-MORB volcanism, which shows higher Pb isotope ratios than do N-MORB rocks (Kim et al., 2006).

5.3. Variable sulfur isotopic compositions

The $\delta^{34}\text{S}$ values of sulfide samples from the EPR near 13°N, 11°N, and 1–2°S, LHF, MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF vary from 0.0 to 9.6‰. The variation in the sulfur isotope compositions of sulfides from different hydrothermal systems is related to the sulfate reduction, the residence time of fluids, and the multiple- stages of hydrothermal activity (e.g., Shanks and Seyfried, 1987; Bluth and Ohmoto, 1988; Peter and Shanks, 1992; Knott et al., 1995, 1998). Sulfate

reduction is favored during slow seawater–fluid mixing in the chimney walls or within a mound, with isotopic fractionation approaching equilibrium values, and ^{34}S -enriched sulfide is produced by the reduction of seawater sulfate during subsurface reaction with ferrous iron-bearing minerals (Peter and Shanks, 1992), implying that the sulfate reduction homogenizes the sulfur isotopic composition of sulfides. Furthermore, the longer residence time of fluids in a hydrothermal system such as TAG might lead to more extensive local sulfate reduction (Knott et al., 1998). Therefore, the change in the $\delta^{34}\text{S}$ values of sulfide samples from the EPR near $1\text{--}2^\circ\text{S}$ (3.0 to 5.8‰, see Table 2), and area A (0.0 to 7.0‰, see Table 2) is attributed to the increased contribution of H_2S derived from reduction of seawater sulfate in the subsurface hydrothermal zone, compared to the H_2S solely leached from the host basalt in deeper parts of the hydrothermal system. In addition, the variations in the $\delta^{34}\text{S}$ values of the sulfides were probably caused by rapid chemical reactions of dissolution, reprecipitation, and replacement (e.g., anhydrite is replaced by sulfide with high $\delta^{34}\text{S}$ values inherited for the seawater) between hydrothermal fluids and earlier sulfide and sulfate minerals in the hydrothermal sulfide deposits, rather than by kinetic isotope effects during precipitation of hydrothermal sulfides (Shanks and Seyfried, 1987; Bluth and Ohmoto, 1988). Furthermore, in the EPR near 13°N , LHF, EHF, KHF, and S99HF, the $\delta^{34}\text{S}$ values of pyrite, chalcopyrite, and sphalerite minerals are strikingly similar (Table 2), indicating a constant sulfur source and a very similar precipitation mechanism (Shanks and Bischoff, 1980). The similarities suggest that the pyrite, chalcopyrite, and sphalerite minerals are formed by a single-stage

hydrothermal fluid. The sulfur source and sulfide producing reactions must have been very similar during the single-stage hydrothermal mineralization.

In addition, the variations in the sulfur isotopic compositions of sulfides or sulfate can be studied by using the discrete degree and variation rate:

$$\delta^{34}\text{S discrete degree (\%)} = [\sum(\delta^{34}\text{S}_i - \delta^{34}\text{S}_{\text{ave}})/(n - 1)]^{0.5}/\delta^{34}\text{S}_{\text{ave}} \quad (1)$$

where $i=1, 2, 3, n$; n is the sample number; and $\delta^{34}\text{S}_{\text{ave}} = \sum(\delta^{34}\text{S})_i / n$;

$$\delta^{34}\text{S variation rate (\%)} = (\delta^{34}\text{S}_{\text{max}} - \delta^{34}\text{S}_{\text{min}}) / \delta^{34}\text{S}_{\text{ave}} \quad (2)$$

where $\delta^{34}\text{S}_{\text{max}}$ is the maximum value of sulfur isotope compositions in sulfide or sulfate samples from the same hydrothermal field, $\delta^{34}\text{S}_{\text{min}}$ is the minimum value of sulfur isotope compositions in sulfide or sulfate samples from the same hydrothermal field, and $\delta^{34}\text{S}_{\text{ave}}$ is the average value of sulfur isotope ratios in sulfide or sulfate samples from the same hydrothermal field.

The discrete degree and variation rate in the sulfur isotope compositions of sulfides from the super-slow, and slow spreading (full spreading rate <50 mm/yr) MORs are larger than those from the super-fast and fast spreading (full spreading rate >80 mm/yr) MORs (Fig. 8). Further, the ranges of sulfur isotopic compositions of sulfides in the super-slow ($\delta^{34}\text{S}$ values 0.0 to 7.0‰, area A), and slow ($\delta^{34}\text{S}$ values 4.5 to 9.6‰, LHF) spreading MORs are larger than those in the super-fast ($\delta^{34}\text{S}$ values 3.0 to 5.8‰, EPR near 1–2°S) and fast ($\delta^{34}\text{S}$ values 0.4 to 5.0‰, EPR near 13°N) spreading MORs (Fig. 9, Table 3).

The large variation in the sulfur isotopic composition of the sulfides in the super-slow, and slow spreading MORs can be explained by the multi-sulfur sources (seawater,

basalt, serpentized peridotite, mafic material, magmatic degassing, sediment) of sulfides (such as in the Guaymas Basin and the Middle Valley in sediment-hosted, slow-spreading MORs, Lau basin) (Shanks and Niemitz, 1982; Koski et al., 1988; Peter and Shanks, 1992; Zierenberg et al., 1993; Duckworth et al., 1994; Zierenberg, 1994; Herzig et al., 1998a). In addition, the degree of fluid–basalt interaction, and/or fluid–seawater mixing are recorded in sulfides as a gradual shift to decreasing (close to 0‰), or increasing (close to 21‰) $\delta^{34}\text{S}$ values, respectively (Fig. 10). The larger (>50%) or smaller (<50%) basalt/seawater sulfur ratios indicate that the majority of sulfur in the sulfide samples is from basalt or seawater, respectively. In the super-fast and fast spreading MORs, the majority of basalt/seawater sulfur ratios in the sulfides are from 70 to 100%, suggesting that the sulfur isotope compositions of sulfides are controlled by the degree of fluid–basalt interaction and fluid–seawater mixing (Fig. 10). In the super-slow, slow, and intermediate spreading ridges, the variation of basalt/seawater sulfur ratios in sulfides range from 40 to >100% (Fig. 10). The larger basalt/seawater sulfur ratios (>100%) in sulfides can result from the magmatic degassing and/or bacterial activity (Fig. 10), as the magmatic degassing and/or bacterial activity can cause the $\delta^{34}\text{S}$ values of sulfides to be lower than 0‰, for example, sulfides in the Hine Hina hydrothermal field (full spreading rate 60 mm/yr) of Lau Basin (Herzig et al., 1998a) and the Guaymas Basin hydrothermal systems (full spreading rate 45 mm/yr) (Peter and Shanks, 1992).

5.4. Variable lead isotopic compositions

The variability of basaltic Pb isotope composition along the mid-ocean ridges is a major cause of Pb isotopic variations in associated seafloor hydrothermal sulfides (Church and Tatsumoto, 1975; Tatsumoto, 1978; Sun, 1980; Vidal and Clauer, 1981; Hamelin et al., 1984). At the EPR near 13°N and 1–2°S, the EHF, the CIR near 25°S, and the S99HF, the range of Pb-isotope compositions in the sulfides is much smaller than in basalts (Figs. 4–7), and the Pb isotopic ratios of sulfides show only minor variations (Table 4), suggesting a common source for the Pb of all sulfides from the EPR near 13°N, the EPR near 1–2°S, the EHF, the area A, and the S99HF.

The variations in the Pb isotopic compositions of sulfides can also be studied by using the discrete degree and variation rate:

$$\text{Pb discrete degree (\%)} = \{\sum[(\text{Pb})_i - (\text{Pb})_{\text{ave}}]/(n - 1)\}^{0.5}/(\text{Pb})_{\text{ave}} \quad (3)$$

where $\text{Pb} = {}^{206}\text{Pb}/{}^{204}\text{Pb}$, ${}^{207}\text{Pb}/{}^{204}\text{Pb}$, and ${}^{208}\text{Pb}/{}^{204}\text{Pb}$; $I = 1, 2, 3$, n ; n is the sample number; $(\text{Pb})_{\text{ave}} = \sum(\text{Pb})_i / n$.

$$\text{Pb variation rate (\%)} = (\text{Pb}_{\text{max}} - \text{Pb}_{\text{min}})/\text{Pb}_{\text{ave}} \quad (4)$$

where Pb_{max} is the maximum ratio of Pb isotope compositions in the sulfide samples from the same hydrothermal field, Pb_{min} is the minimum ratio of Pb isotope compositions in the sulfide samples from the same hydrothermal field, and Pb_{ave} is the average value of Pb isotope ratios in sulfide samples from the same hydrothermal field.

There is no clear relationship between the variation rate in the Pb isotope compositions of sulfides from different ridge segments and the local spreading rate of the mid-ocean ridge, suggesting that the spreading rate of a mid-ocean ridge does not

significantly affect the Pb isotopic compositions in the sulfides from a local hydrothermal field.

The variation in the Pb isotope compositions of sulfides from different hydrothermal systems is related to the Pb sources of sulfides and the residence time of fluids. On the sediment-hosted mid-ocean ridges, the Pb of sulfides may be from three sources: sediment, seawater and volcanic rocks. The Pb isotope ratios of sulfides on such ridges (e.g., Middle Valley, Escanaba Trough) have a larger range than those of sulfides from the sediment-starved mid-ocean ridges (e.g., EPR at 1–2°S, EPR at 17°26'S, EPR at 18°31'S; Table 5), and the Pb of sulfides from the sediment-starved mid-ocean ridges is mainly from basaltic rocks. Furthermore, sulfides display significant variations in Pb isotope compositions, such as those from the S99HF. It is likely that hydrothermal fluids percolated through very heterogeneous volcanic sequences formed of both enriched and depleted MORBs, confirming the results of previous studies by Kim et al. (2006).

For the difference in Pb isotope composition for sulfides from the same hydrothermal field, such as in the EHF and LHF (Table 4), a possible explanation is that it has implications for the residence time of subsurface hydrothermal fluid. These variations could be related to different sulfide ages, and it is regrettable that there are no age data for sulfides from the EHF. The age differences of sulfides from the LHF (3,900–60,000 years) (Lalou et al., 1996; Kuznetsov et al., 2006) are insufficient to cause a measurable radiogenic enrichment. We interpret the variations to be a reflection of differences in residence time of subsurface hydrothermal fluid. In the EHF, there is no

evidence to show that a sediment component will lead to hydrothermal fluid and related sulfides that have more radiogenic Pb than found in the present study. Furthermore, it is possible that the initial hydrothermal fluid had different Pb isotope compositions compared with the recently vented hydrothermal fluid because vent fluid evolution is different in different parts of the same hydrothermal field (Yao et al., 2009). Another possible explanation is changing Pb isotope compositions in the hydrothermal fluids. In general, the changes in fluid paths caused by a magmatic/diking event may lead to changes in the chemistry of hydrothermal fluid (Rubin et al., 1994; Von Damm et al., 1995; Fornari et al., 1998; Seyfried et al., 2003). Unfortunately, time-series of Pb isotopic ratios of hydrothermal fluids were not determined in the EHF, and will be the main objective of future studies.

6. Conclusion

The $\delta^{34}\text{S}$ values of sulfide minerals from the EPR near 13°N, 11°N, and 1–2°S, LHF, MAR near 13°S, KHF, EHF, CIR near 25°S, area A, and S99HF vary from 0.0 to 9.6‰, with a mean of 4.7‰, and fall within the $\delta^{34}\text{S}$ value range for sulfide samples ($n = 1841$) from the other seafloor hydrothermal field (1 to 9‰). The $\delta^{34}\text{S}$ values are between those of the seawater and the igneous rocks, such as basalt, serpentinized peridotite, and mafic material, suggesting that the S in the sulfide samples is a mixture of that derived from igneous rocks and seawater, but mainly leached from igneous rocks. In the area A, the $\delta^{34}\text{S}$ values of pyrite minerals exhibit a larger variation range

(from 0.0 to 7.0‰), suggesting that the pyrite minerals are formed by multi-stage hydrothermal fluids. In addition, on the EPR near 1–2°S, EHF, and S99HF, not one of the five measured pyrite–sphalerite pairs, or four measured pyrite–chalcopyrite pairs falls within the range of equilibrium temperatures.

The Pb isotopic compositions of seafloor hydrothermal sulfides from the EPR near 13°N and 1–2°S, MAR near 13°S, EHF, CIR near 25°S, area A, and S99HF were very homogenous and defined a narrow range, falling in the field of the large Pb isotopic dataset from the EPR, MAR, IR, and NFB basalts, respectively, suggesting that the Pb in the sulfides is derived predominantly from basaltic rocks. In addition, the variations in the S and Pb isotopic compositions of sulfides can be studied using the discrete degree and variation rate, and the variation in the S and Pb isotope compositions of sulfides from deep-sea hydrothermal systems is controlled by the sulfur and lead sources, in combination with the fluid processes including fluid–rock interaction, fluid–seawater mixing and residence time of subsurface hydrothermal fluid.

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Figure Captions

Fig. 1. Locations of seafloor hydrothermal sulfide samples from deep-sea hydrothermal fields analyzed for sulfur and lead isotopic compositions in this study. KHF–Kairei hydrothermal field; EHF–Edmond hydrothermal field; CIR–Central Indian Ridge; SWIR–Southwest Indian Ridge; S99HF–Sonne 99 hydrothermal field; NFB–North Fiji Basin; EPR–East Pacific Rise; LHF–Logatchev hydrothermal field; MAR–Mid-Atlantic Ridge.

Fig. 2. Histogram of sulfur isotope values for sulfide samples from A: EPR near 1–2°S and 11°N; B: EPR near 13°N, LHF, EHF, and MAR near 13°S; C: KHF, CIR near 25°S, and area A; D: S99HF and other hydrothermal fields (including EPR near 21°S, 16°43'S, 7°24'S, 1–2°S, 9–10°N, 11°N, 13°N, and 21°N; Galapagos Rift; southern Juan de Fuca Ridge (SJdFR); Axial Seamount; Lucky Strike; Rainbow; Broken Spur; TAG; Snake Pit; LHF; MAR near 13°S; EHF; KHF; CIR near 25°S; area A on the SWIR; Middle Valley; Escanaba Trough; Guaymas Basin; Red Sea; Jade hydrothermal field; Mariana Trough; Manus Basin; NFB; Lau Basin; Myojinsho caldera; Conical Seamount; and Brothers Seamount). Sources of sulfur isotope data are in Table 2 and references are in Table 3.

Fig. 3. Sulfur isotope values for sulfide samples from different hydrothermal fields (including EPR near 21°S, 16°43'S, 7°24'S, 1–2°S, 9–10°N, 11°N, 13°N, and 21°N; Galapagos Rift; SJdFR; EHF; KHF; Lucky Strike; Rainbow; Broken Spur; TAG;

Snake Pit; LHF; area A; Middle Valley (MV); Escanaba Trough; Guaymas Basin; Jade; Mariana Trough; Manus Basin; North Fiji Basin; Lau Basin; Brothers Seamount; Myojinsho caldera; Conical Seamount; Red Sea; and Axial Seamount). Sources of sulfur isotope data are in Table 2 and references are in Table 3. MORB data are from Sakai et al. (1984), Alt et al. (1989), Shanks et al. (1995), and Alt and Shanks (2003). Vent fluid data are from Michard et al. (1984), Merlivat et al. (1987), Von Damm and Bischoff (1987), Campbell et al. (1988), Bluth and Ohmoto (1988), Bowers et al. (1988), Massoth et al. (1989), Butterfield et al. (1990), Shanks et al. (1995), and Shanks (2001). Seawater data is from Rees et al. (1978).

Fig. 4. A: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; B: $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plots for hydrothermal sulfides from EPR near 13°N and 1–2°S. EPR near 13°N basalts, EPR near 1–5°S basalt, and EPR MORB are from the updated PetDB database (<http://www.petdb.org>). Fe-Mn crust data are from Von Blanckenburg et al. (1996). FMCA is average value of the Pb isotope ratios in Fe-Mn crust. EPRBA is average value of the Pb isotope ratios in EPR near 13°N basalts. ML is mixing line between Pb isotope compositions of FMCA and EPRBA, and mixing line between Pb isotope compositions of FMCA and EPR near 1–5°S basalt. NHRL is Northern Hemisphere Reference Line (Hart, 1984). Maximum 2σ error for all sulfide samples is also plotted.

Fig. 5. A: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; B: $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plots for hydrothermal sulfides from Logatchev hydrothermal field and MAR near 13°S.

Ultramafic rocks, MAR near 14°N basalts, MAR near 13°S basalt, and MAR MORB are from the updated PetDB database (<http://www.petdb.org>). Fe-Mn crust data are from Von Blanckenburg et al. (1996). Sediments data are from Ben Othman et al. (1989). NHRL is Northern Hemisphere Reference Line (Hart, 1984). Maximum 2 σ error for all sulfide samples is also plotted.

Fig. 6. A: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; B: $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plots for hydrothermal sulfides from Edmond hydrothermal field, Kairei hydrothermal field, CIR near 25°S, and area A on the SWIR. The data for CIR near 24°S basalts, CIR near 25°S basalt, SWIR near 37°S basalts, and IR MORB are from the updated PetDB database (<http://www.petdb.org>). Fe-Mn crust data are from Von Blanckenburg et al. (1996) and Vlastélic et al. (2001). FMCA is average value of Pb isotope ratios in Fe-Mn crust. CIRBA is average value of Pb isotope ratios in CIR near 25°S basalts. ML is mixing line between Pb isotope compositions of FMCA and CIRBA. NHRL is Northern Hemisphere Reference Line (Hart, 1984). Maximum 2 σ error for all sulfide samples is also plotted.

Fig. 7. A: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; B: $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plots for hydrothermal sulfides from S99HF. Fe-Mn crust data are from Von Blanckenburg et al. (1996). NHRL is Northern Hemisphere Reference Line (Hart, 1984). North Fiji Basin basalts data are from Kim et al. (2006). Maximum 2 σ error for all sulfide samples is also plotted.

Fig. 8. A: $\delta^{34}\text{S}$ discrete degree vs. spreading rate; B: $\delta^{34}\text{S}$ variation vs. spreading rate plots for hydrothermal sulfides from different seafloor hydrothermal systems. Sources of sulfur isotope data in sulfides are in Table 2 and references are in Table 3.

Fig. 9. Plots of $\delta^{34}\text{S}$ vs. spreading rate for hydrothermal sulfides from different seafloor hydrothermal systems. Sources of sulfur isotope data in sulfides are in Table 2 and references are in Table 3.

Fig. 10. Basalt/seawater sulfur ratio vs. spreading rate plots for hydrothermal sulfides from different seafloor hydrothermal systems. Basalt/seawater sulfur ratio (%) = $(\delta^{34}\text{S}_{\text{seawater}} - \delta^{34}\text{S}_s) / (\delta^{34}\text{S}_{\text{seawater}} - \delta^{34}\text{S}_{\text{basalt}})$, where $\delta^{34}\text{S}_{\text{seawater}} = 21\text{‰}$ (Rees et al. 1978), $\delta^{34}\text{S}_{\text{basalt}} = 0.1\text{‰}$ (Sakai et al. 1984), and $\delta^{34}\text{S}_s$ is sulfur isotope ratios in sulfide samples from different seafloor hydrothermal systems. Sources of sulfur isotope data in sulfides are in Table 2 and references are in Table 3.

Table Headings

Table 1 Description of seafloor massive sulfide samples for sulfur and lead isotopic

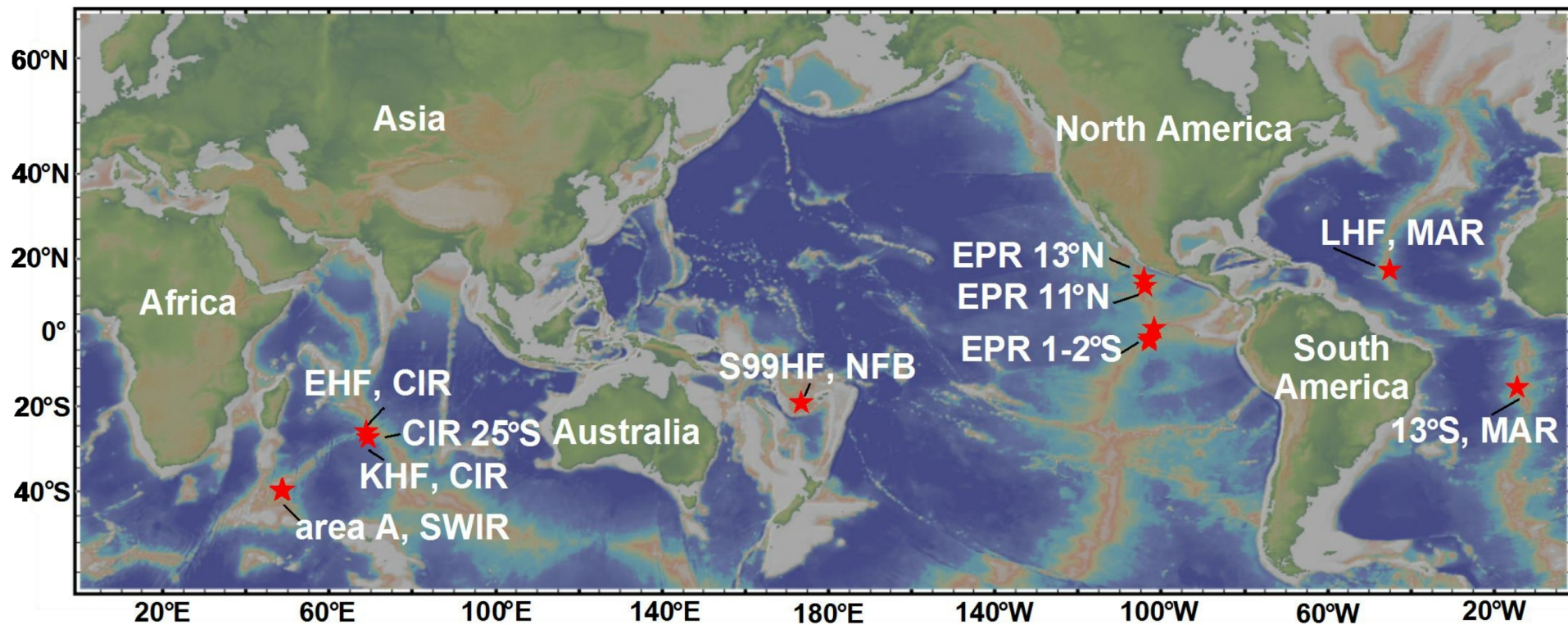
compositions in this study.

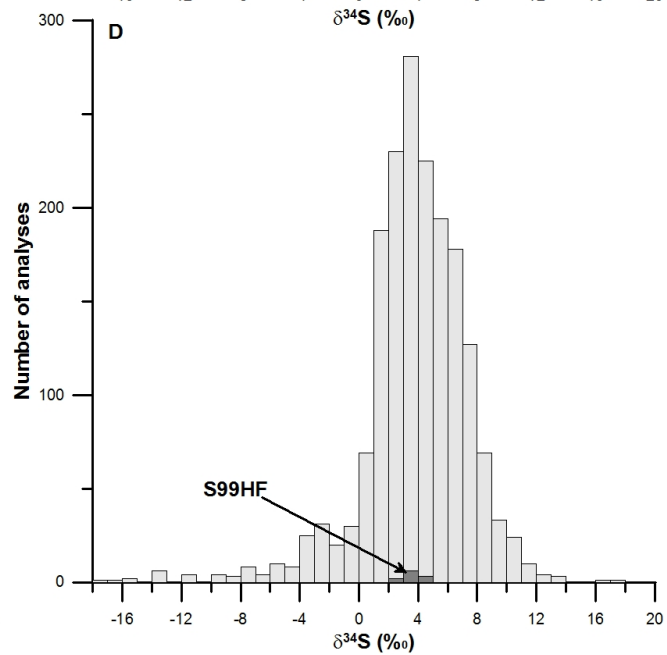
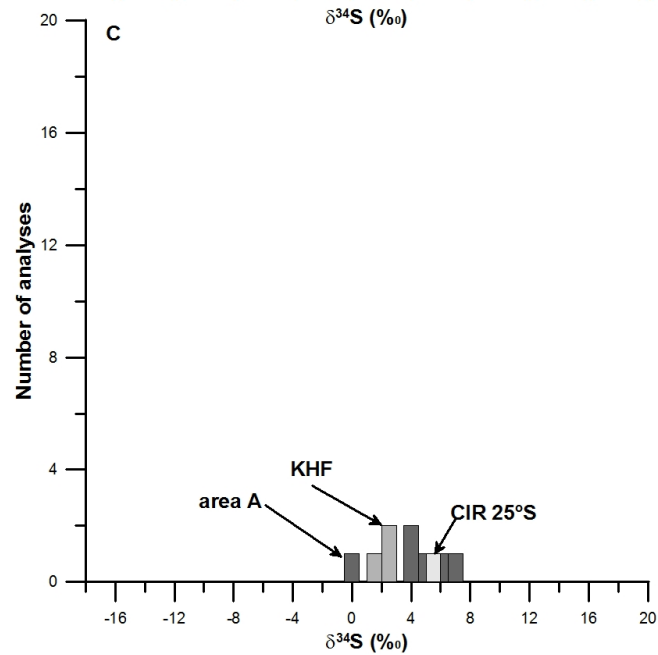
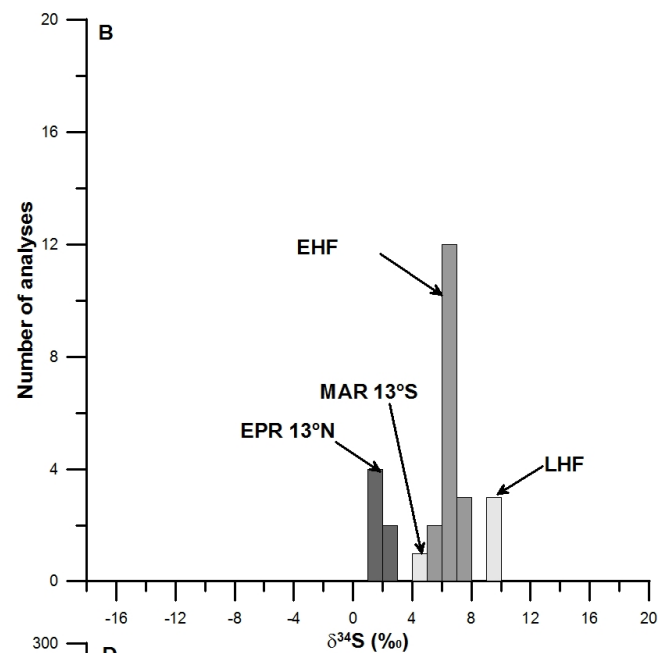
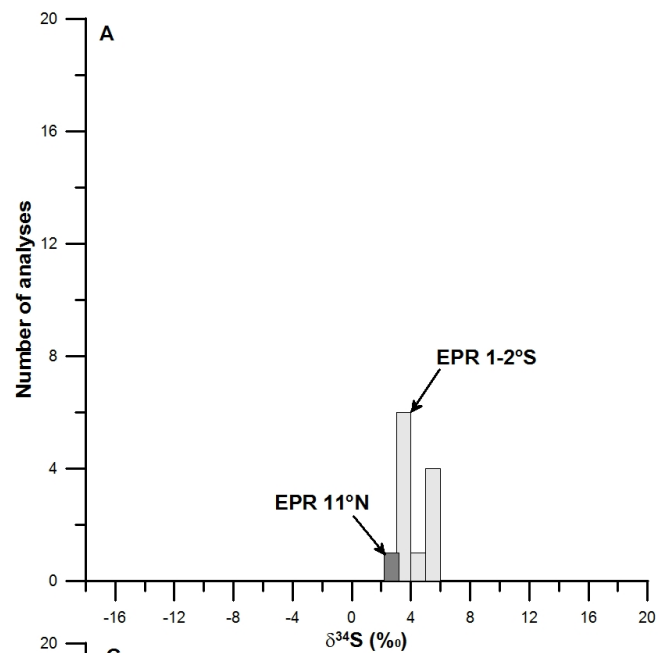
Table 2 Sulfur isotopic compositions of seafloor hydrothermal sulfide and sulfate minerals from the EPR near 1–2°S, 13°N and 11°N, KHF, CIR near 25°S, EHF, LHF, MAR near 13°S, area A, and S99HF.

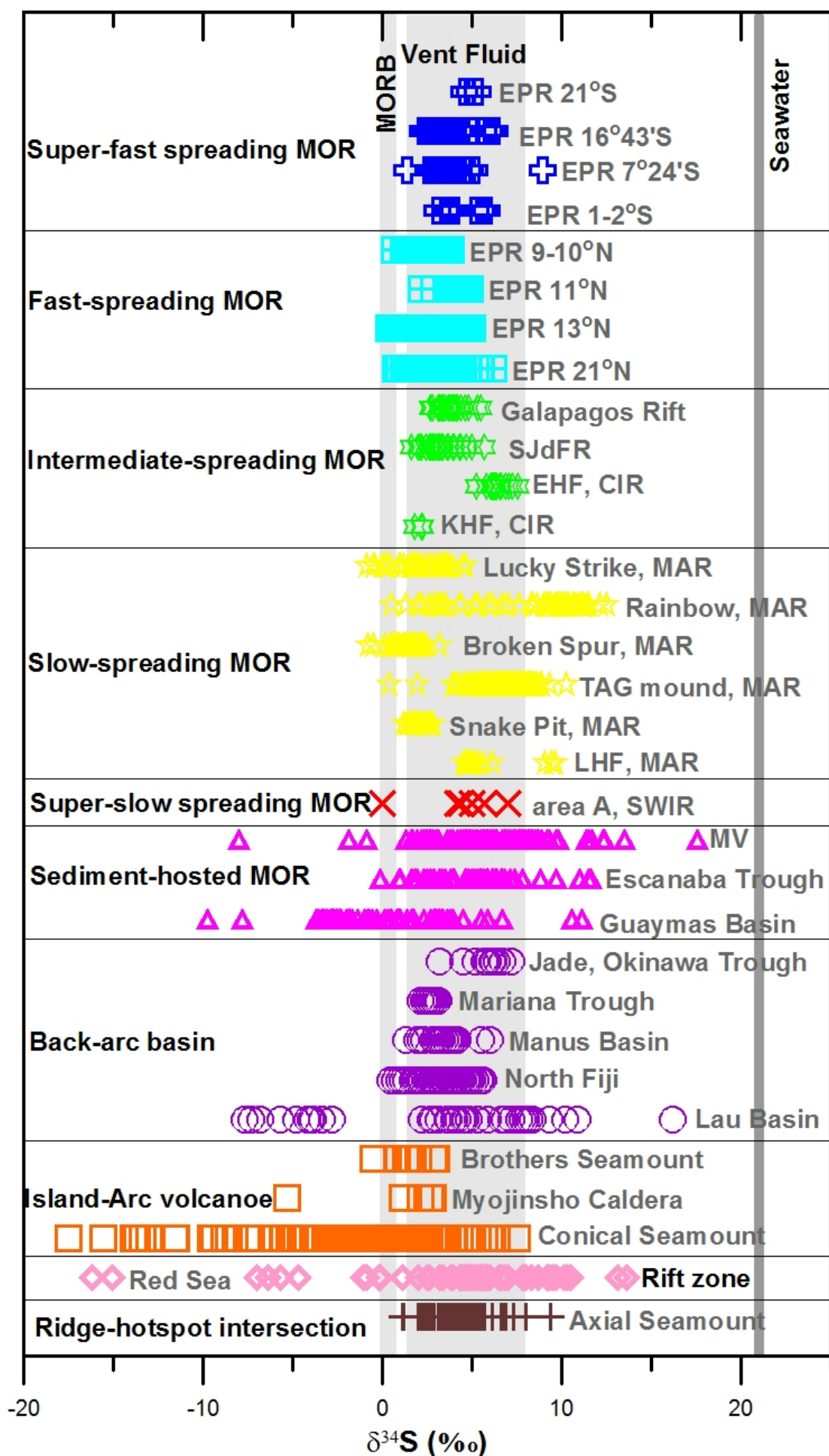
Table 3 Comparison of sulfur isotopic compositions of seafloor hydrothermal sulfides from different deep-sea hydrothermal systems.

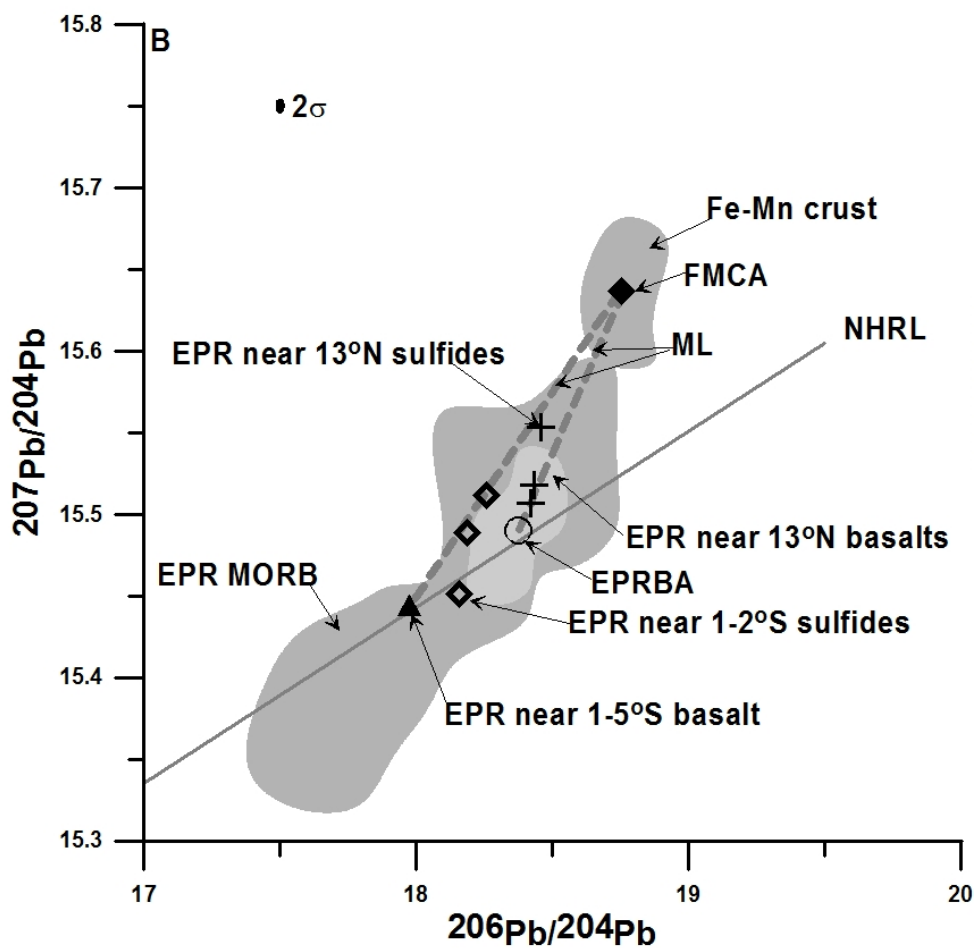
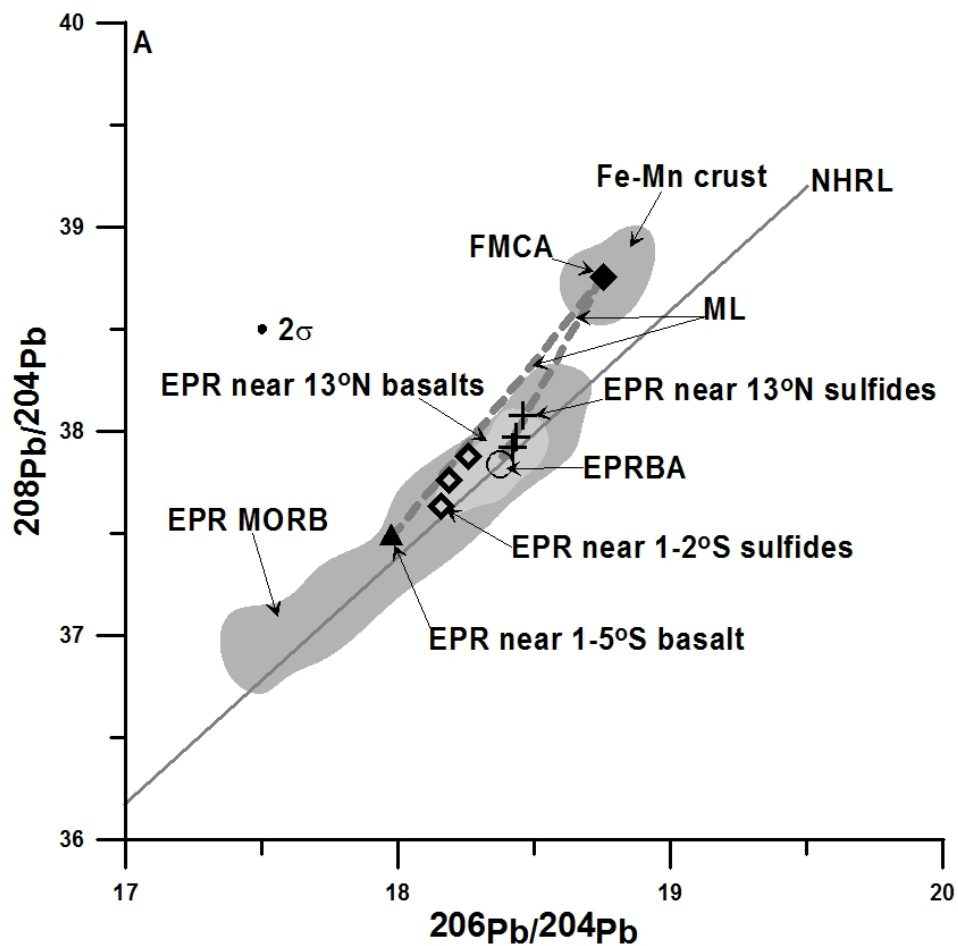
Table 4 Lead isotopic compositions of seafloor massive sulfide samples from EPR near 1–2°S and 13°N, KHF, CIR near 25°S, EHF, LHF, MAR near 13°S, area A, and S99HF.

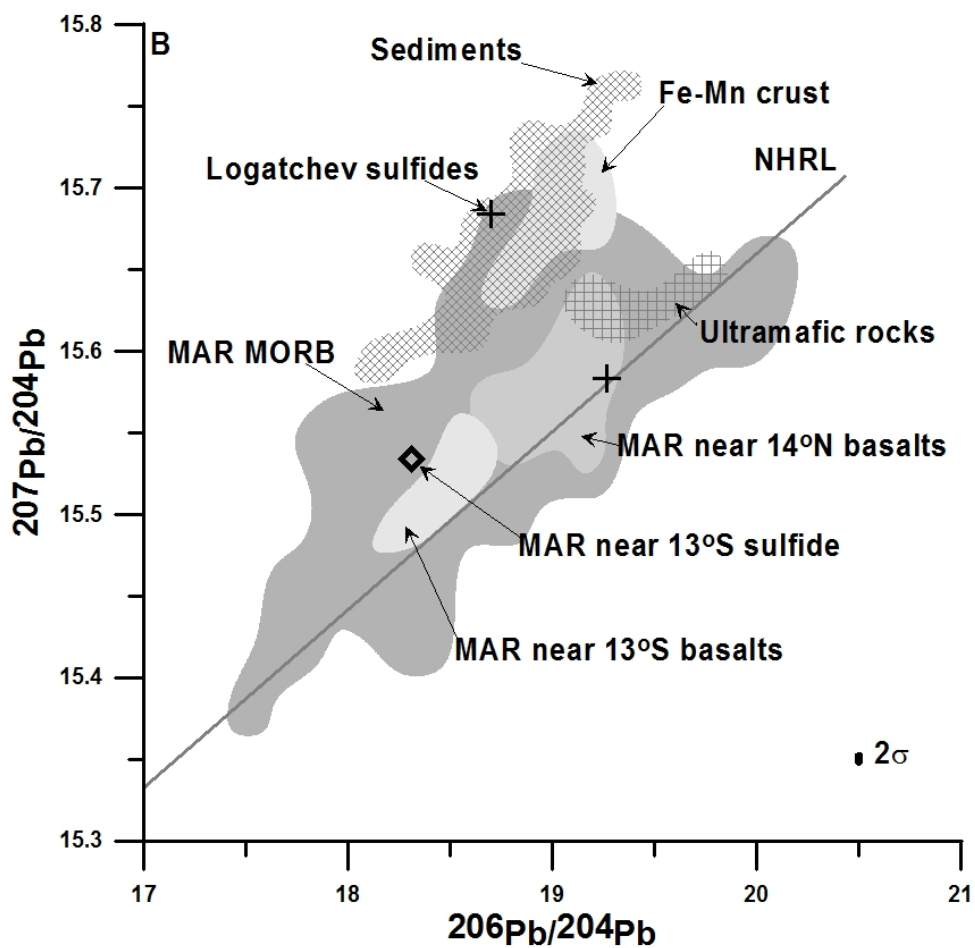
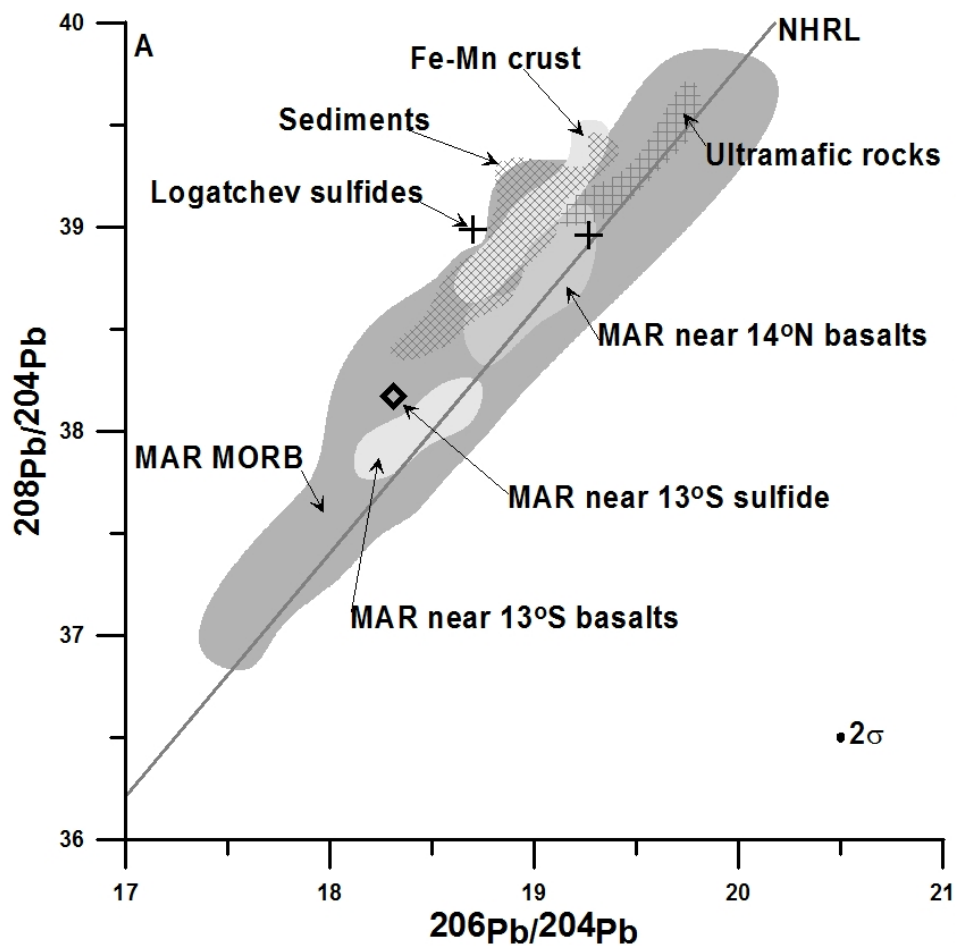
Table 5 Comparison of Pb isotope compositions of seafloor massive sulfides from different deep-sea hydrothermal systems.

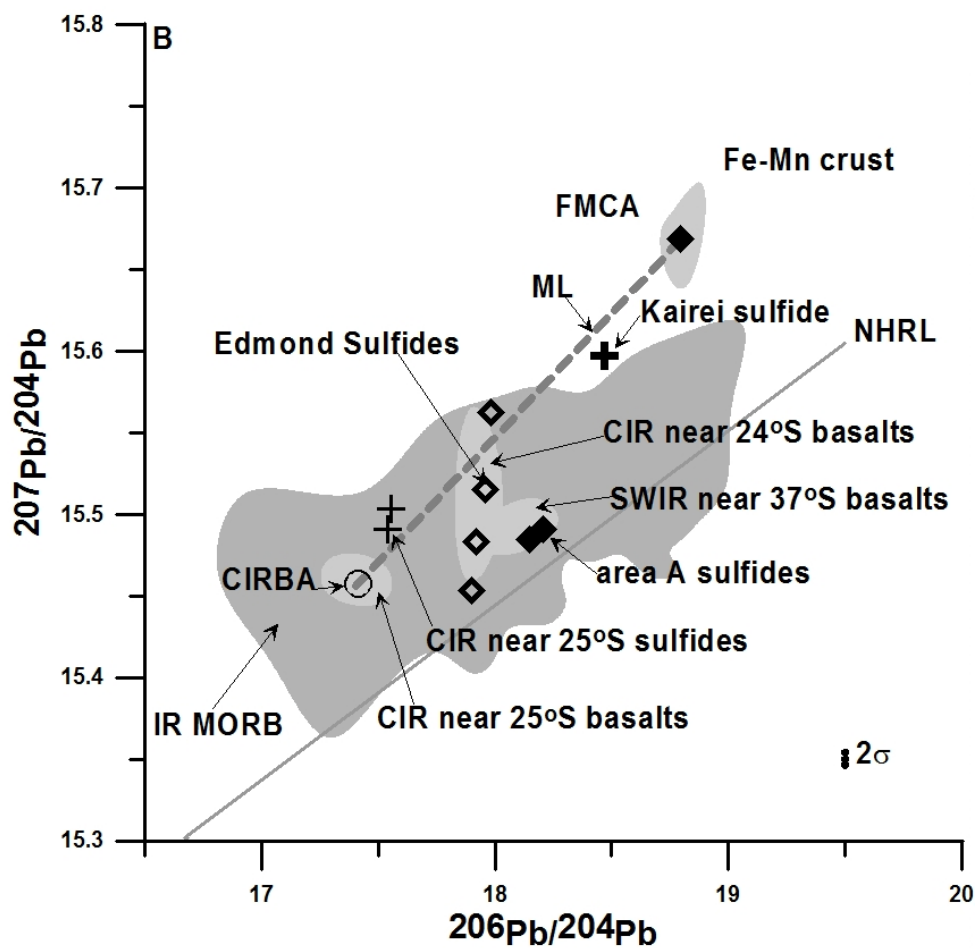
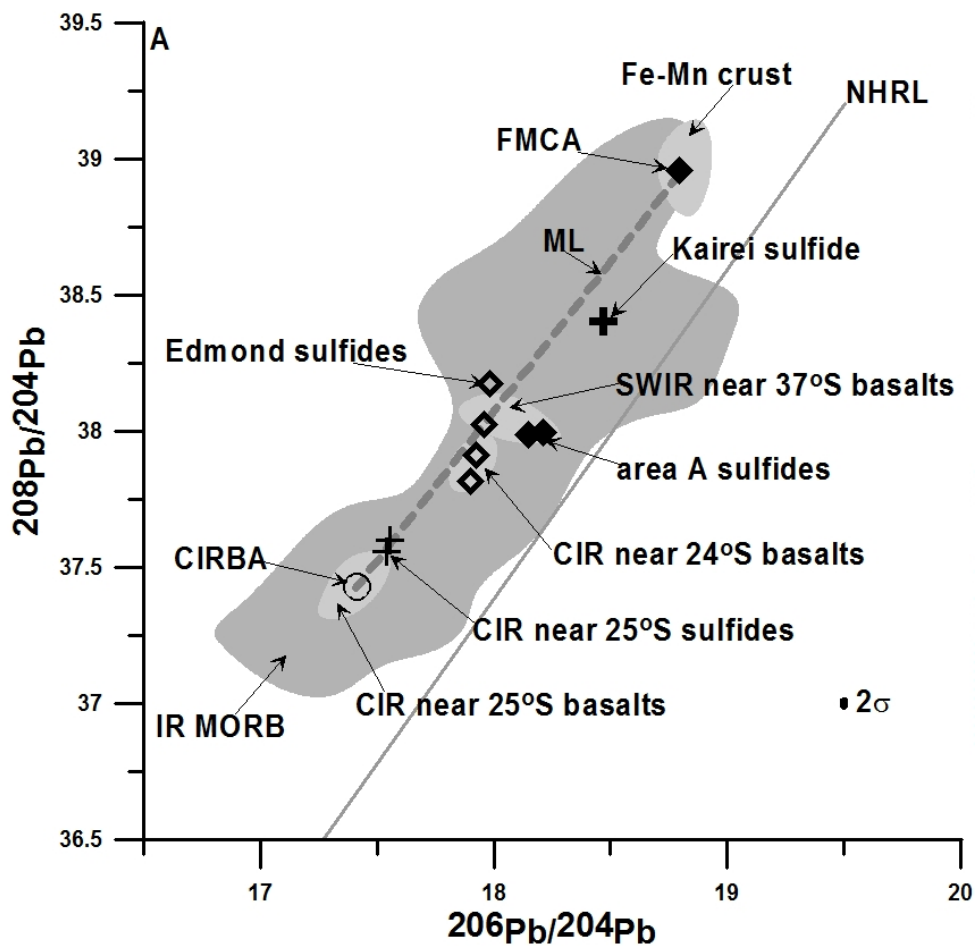


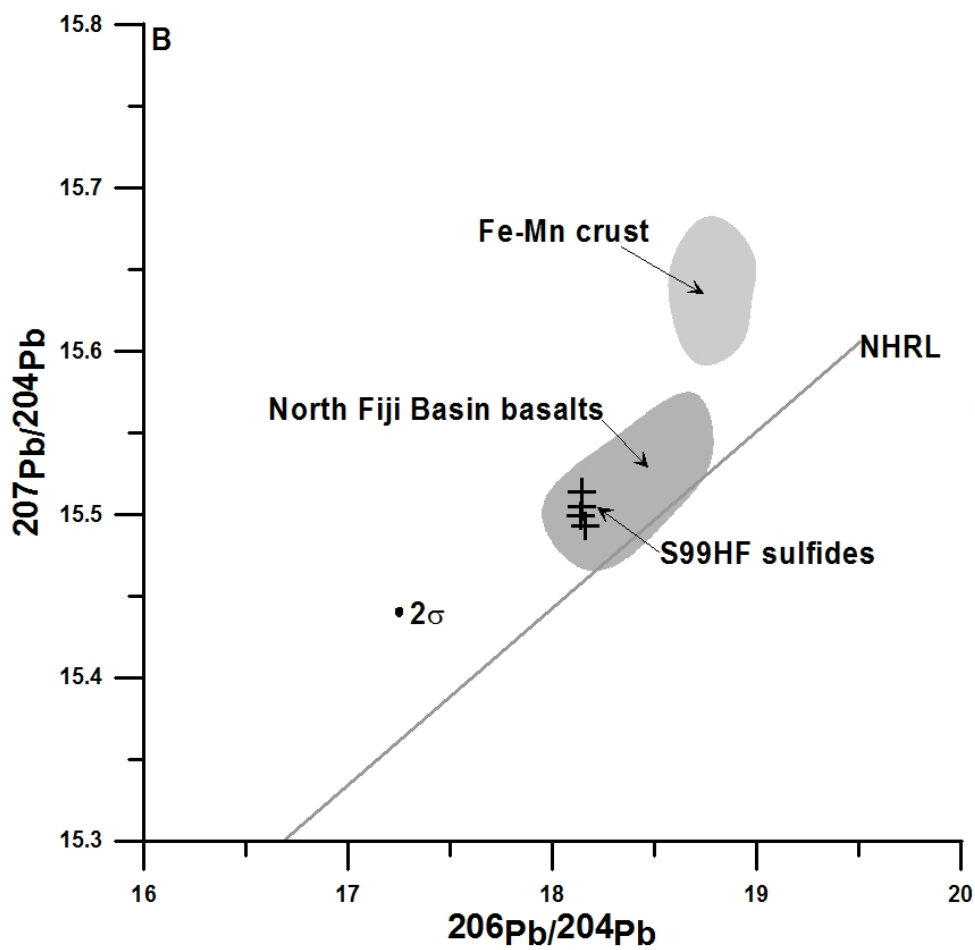
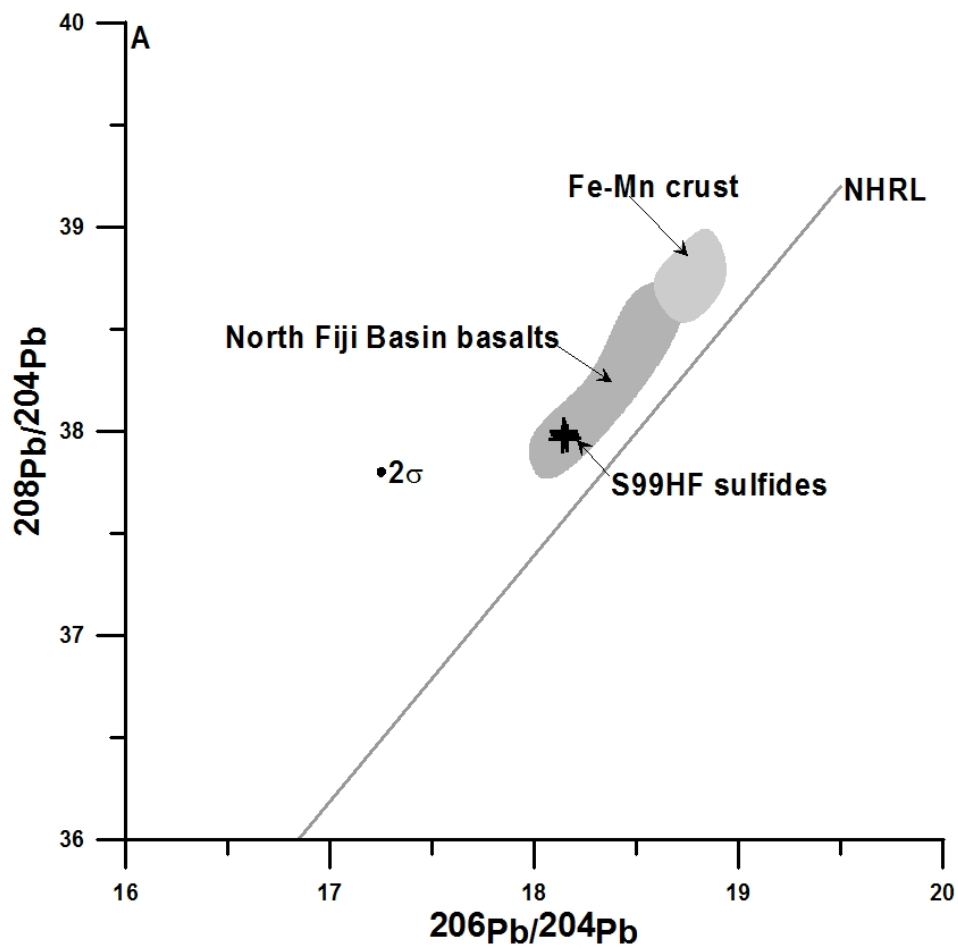


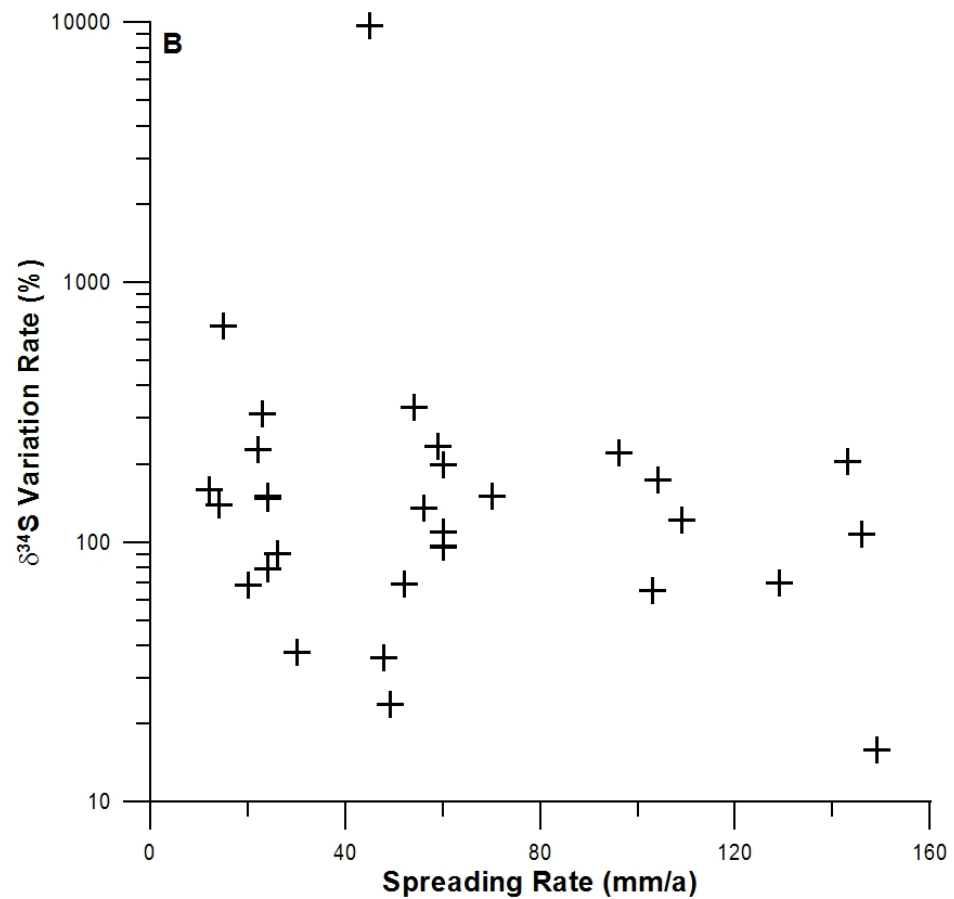
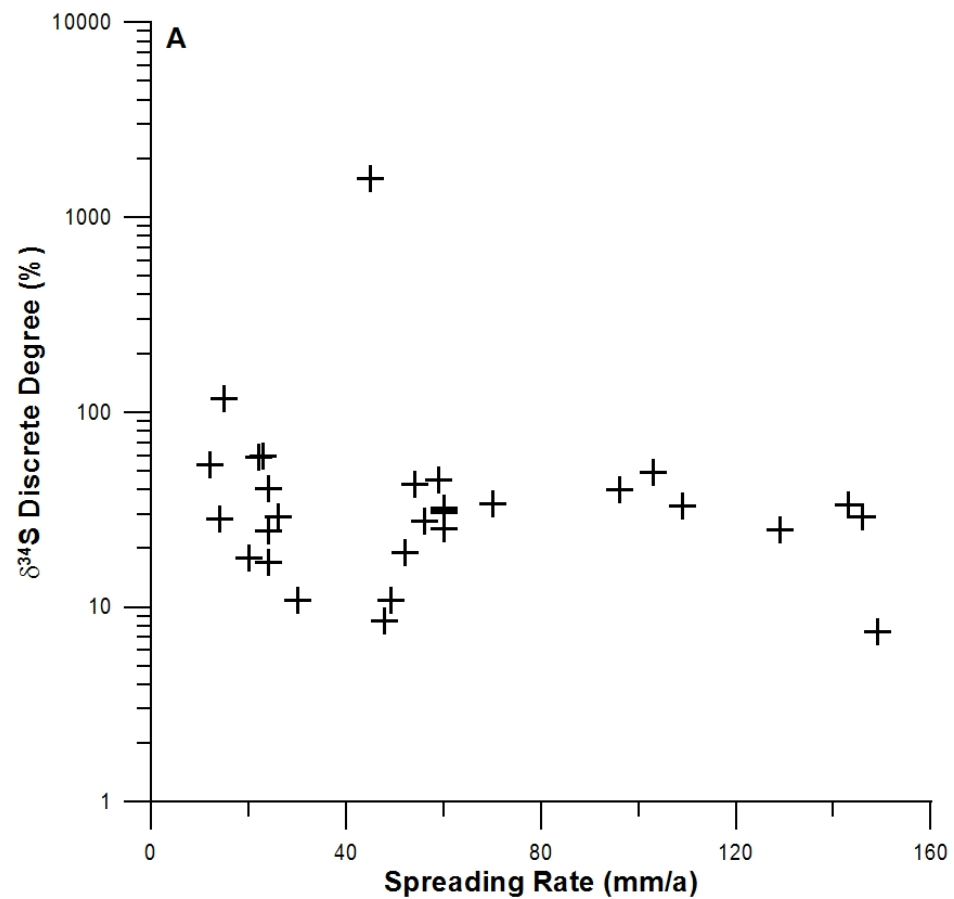


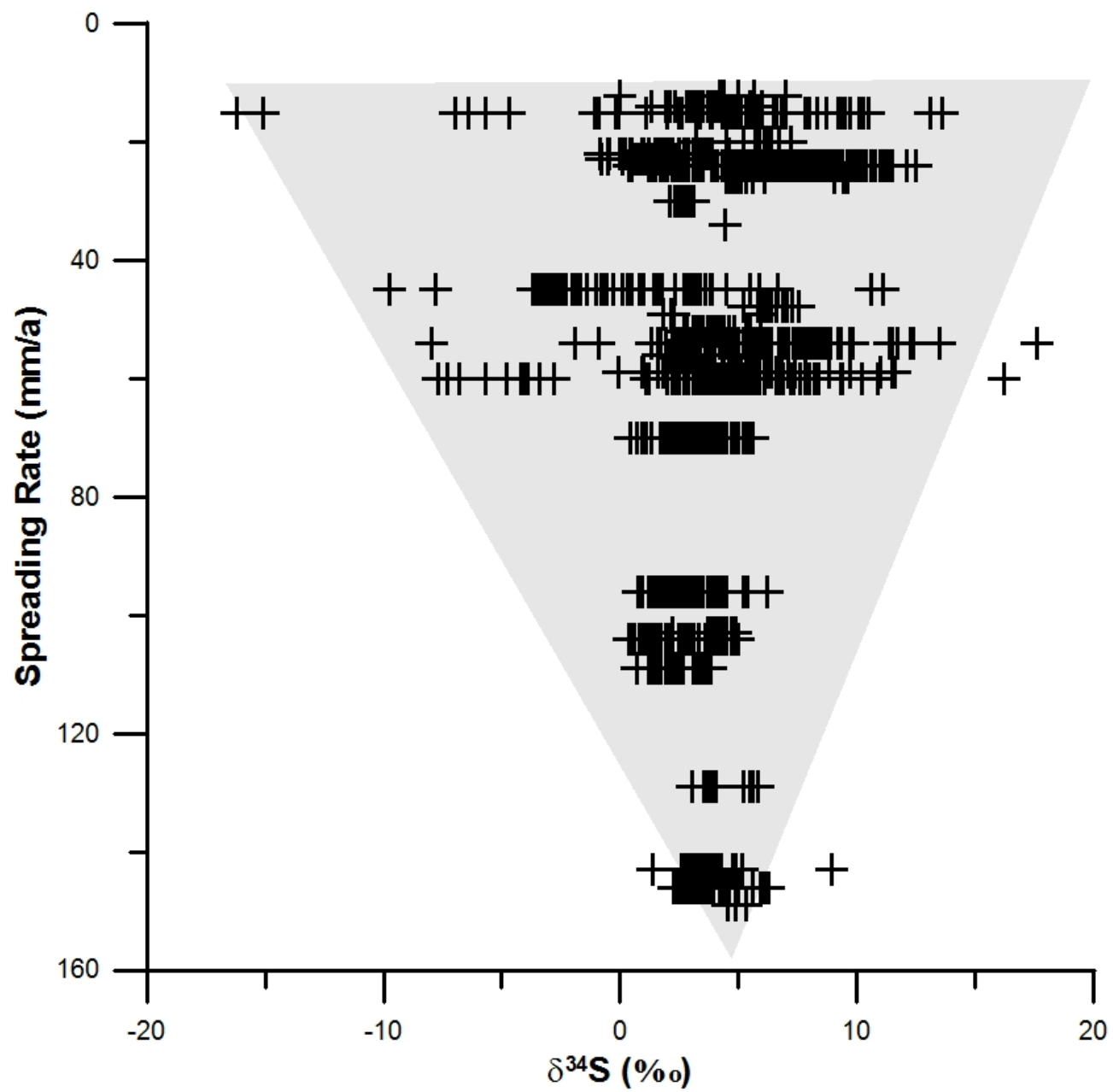












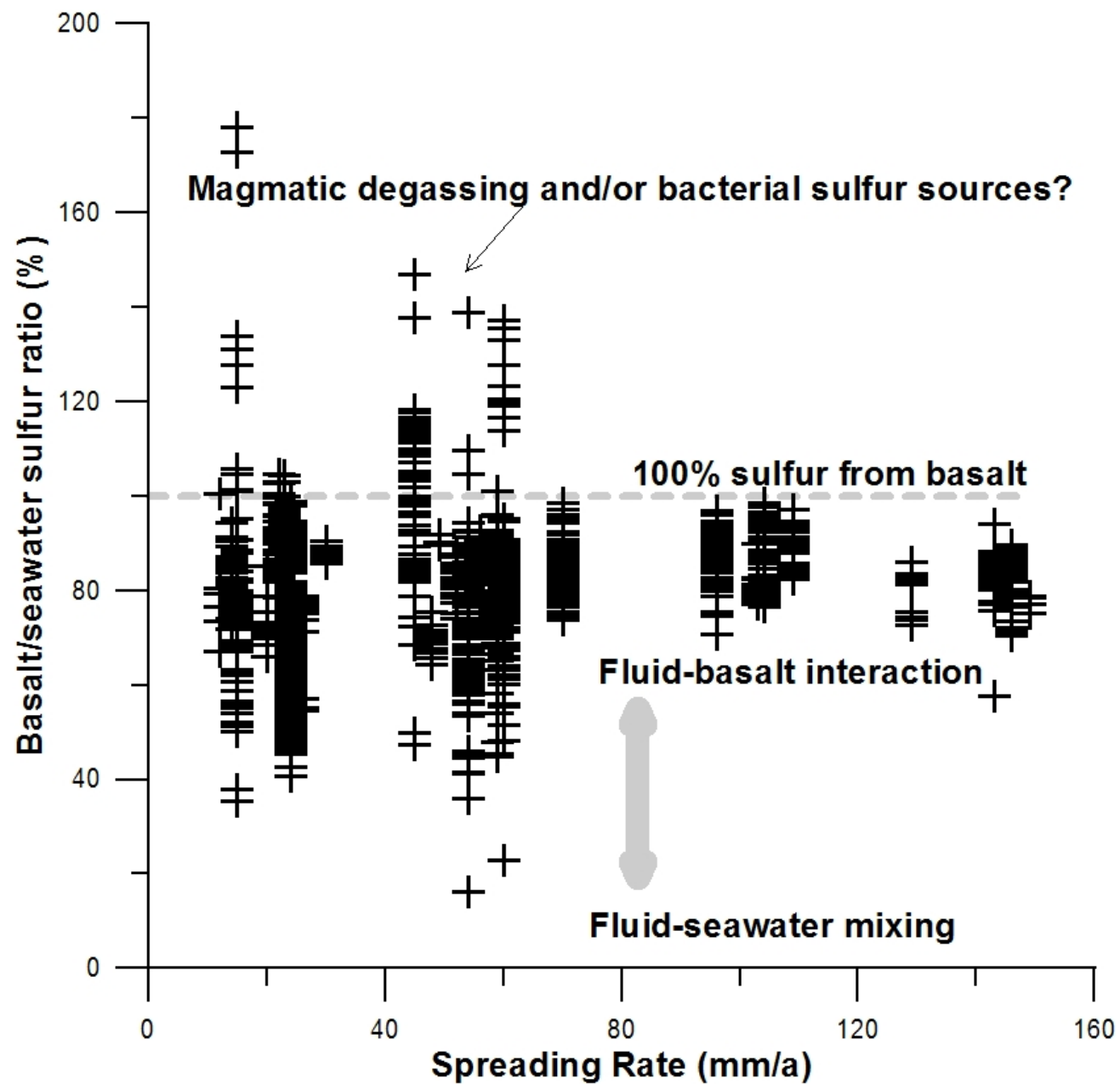


Table 1 Description of seafloor massive sulfide samples for sulfur and lead isotopic compositions in this study.

| Field | Sample No. | Latitude | Longitude | Water depth (m) | Basement rocks | Description | Sulfide mineralogy |
|---|-------------------|------------|--------------|--------------------|-------------------|---|-----------------------------|
| <i>Ultra-fast spreading mid-ocean ridge</i> | | | | | | | |
| 1–2°S, EPR | 20III-S4-TVG1-1-1 | 1°22.130′S | 102°37.360′W | 2,747 | Basalts | Porous chimney fragment coated with tan Fe hydroxides and partially filled conduits | Py +++; Mc +, Cpy +; Sp + |
| 1–2°S, EPR | 20III-S4-TVG1-1-2 | 1°22.130′S | 102°37.360′W | 2,747 | Basalts | Porous chimney fragment coated with tan Fe hydroxides and partially filled conduits | Py +++; Mc +, Cpy +; Sp + |
| 1–2°S, EPR | 20III-S4-TVG1-1-3 | 1°22.130′S | 102°37.360′W | 2,747 | Basalts | Porous chimney fragment coated with tan Fe hydroxides and partially filled conduits | Py +++; Mc +, Cpy +; Sp + |
| 1–2°S, EPR | 20III-S4-TVG1-1-4 | 1°22.130′S | 102°37.360′W | 2,747 | Basalts | Porous chimney fragment coated with tan Fe hydroxides and partially filled conduits | Py +++; Mc +, Cpy +; Sp + |
| 1–2°S, EPR | 20III-S4-TVG1-2-1 | 1°22.130′S | 102°37.360′W | 2,747 | Basalts | Chimney fragment coated with tan Fe hydroxides | Py +++; Cpy ++; Mc ++; Sp + |
| 1–2°S, EPR | 20III-S4-TVG1-2-2 | 1°22.130′S | 102°37.360′W | 2,747 | Basalts | Chimney fragment coated with tan Fe hydroxides | Py +++; Cpy ++; Mc ++; Sp + |
| 1–2°S, EPR | 20III-S4-TVG1-2-3 | 1°22.130′S | 102°37.360′W | 2,747 | Basalts | Chimney fragment coated with tan Fe hydroxides | Py +++; Cpy ++; Mc ++; Sp + |
| 1–2°S, EPR | 20III-S6-TVG3 | 2°09.102′S | 102°38.760′W | 2,921 | Basalts | Outer chimney wall fragment coated with red | Mc ++, Py +++; Sp ++; Cpy + |

| | | | | | | | |
|---------------------------------------|-----------------|-------------|--------------|-------|---------|--|------------------------------|
| | | | | | | brown Fe hydroxides and white anhydrite layer | |
| 1–2°S, EPR | 21III-S17-TVG13 | 0°50.226′S | 101°27.954′W | 2,899 | Basalts | Outer chimney wall fragment coated with red brown Fe hydroxides and white anhydrite layer | Mc +++, Py +++; Sp ++; Cpy + |
| <i>Fast-spreading mid-ocean ridge</i> | | | | | | | |
| 13°N, EPR | EPR05-TVG1-2-1 | 12°42.669′N | 103°54.426′W | 2,628 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides, and small conduits | Py +++; Sp +, Cpy + |
| 13°N, EPR | EPR05-TVG1-2-2 | 12°42.669′N | 103°54.426′W | 2,628 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides, and small conduits | Py +++; Sp +, Cpy + |
| 13°N, EPR | EPR05-TVG1-2-4 | 12°42.669′N | 103°54.426′W | 2,628 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides, and small conduits | Py +++; Sp +, Cpy + |
| 13°N, EPR | EPR05-TVG1-2-2 | 12°42.669′N | 103°54.426′W | 2,628 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides, and small conduits | Py +++; Sp +, Cpy + |
| 13°N, EPR | EPR05-TVG1-3-2 | 12°42.669′N | 103°54.426′W | 2,628 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides, and oxidized pyrite aggregates | Py +++; Cpy +, Sp + |
| 13°N, EPR | EPR05-TVG1-3-3 | 12°42.669′N | 103°54.426′W | 2,628 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides, and oxidized pyrite aggregates | Py +++; Cpy +, Sp + |
| 13°N, EPR | EPR05-TVG2-1-1 | 12°42.678′N | 103°54.414′W | 2,633 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides and many elliptical cavities, showing development of mineral zoning | Py +++, Mc +++; Sp + |
| 13°N, EPR | EPR05-TVG2-1-2 | 12°42.678′N | 103°54.414′W | 2,633 | Basalts | Fe-rich massive sulfides coated with tan Fe | Py +++, Mc +++; Sp + |

| | | | | | | | |
|---|----------------|-------------|--------------|-------|---------|--|----------------------|
| | | | | | | hydroxides and many elliptical cavities, showing development of mineral zoning | |
| 13°N, EPR | EPR05-TVG2-1-4 | 12°42.678'N | 103°54.414'W | 2,633 | Basalts | Fe-rich massive sulfides coated with tan Fe hydroxides and many elliptical cavities, showing development of mineral zoning | Py +++, Mc +++; Sp + |
| 11°N, EPR | 1384-2-2 | 10°56'N | 103°41'W | 2,500 | Basalts | Inactive Zn-rich chimney fragment with yellowish-brown Fe oxides and anhydrite, and Cu-rich inner conduit | Zn +++; Py ++; Cpy + |
| <i>Intermediate-spreading mid-ocean ridge</i> | | | | | | | |
| KHF, CIR | IR05-TVG-9-1 | 25°19.221'S | 70°02.420'E | 2,437 | Basalts | Chimney fragment with finely bladed chalcopyrite | Py +++; Cpy + |
| KHF, CIR | IR05-TVG-9-2 | 25°19.221'S | 70°02.420'E | 2,437 | Basalts | Chimney fragment with finely bladed chalcopyrite | Py +++; Cpy + |
| KHF, CIR | IR05-TVG-9-3 | 25°19.221'S | 70°02.420'E | 2,437 | Basalts | Chimney fragment with finely bladed chalcopyrite | Py +++; Cpy + |
| 25°S, CIR | 19III-S12-TVG6 | 25°09.228'S | 70°04.482'E | 2,443 | Basalts | Porous Cu-rich sulfide fragment with yellowish brown oxides in the cavities, local light green secondary Cu sulfides | Cpy +++; |
| EHF, CIR | IR05-TVG12-5-2 | 23°52.678'S | 69°35.808'E | 3,293 | Basalts | Grey black Zn-rich massive sulfides coated with red to brown oxide crusts, nodular | Sp +++; Py ++, Mc ++ |

| | | | | | | | |
|----------|----------------|-------------|-------------|-------|---------|---|------------------------------|
| | | | | | | structure in the outside | |
| EHF, CIR | IR05-TVG12-8-2 | 23°52.678'S | 69°35.808'E | 3,293 | Basalts | Grey black Zn-rich massive sulfides coated with red to brown oxide crusts, nodular structure in the outside | Sp +++; Py ++, Mc ++ |
| EHF, CIR | IR05-TVG12-8-4 | 23°52.678'S | 69°35.808'E | 3,293 | Basalts | Grey black Zn-rich massive sulfides coated with red to brown oxide crusts, nodular structure in the outside | Sp +++; Py ++, Mc ++ |
| EHF, CIR | IR05-TVG12-9-1 | 23°52.678'S | 69°35.808'E | 3,293 | Basalts | Grey black Zn-rich massive sulfides coated with red to brown oxide crusts, nodular structure in the outside | Sp +++; Py ++, Mc ++ |
| EHF, CIR | IR05-TVG12-11 | 23°52.678'S | 69°35.808'E | 3,293 | Basalts | Grey black Zn-rich massive sulfides coated with red to brown oxide crusts, nodular structure in the outside | Sp +++; Py ++, Mc ++ |
| EHF, CIR | IR05-TVG12-14 | 23°52.678'S | 69°35.808'E | 3,293 | Basalts | Grey black Zn-rich massive sulfides coated with red to brown oxide crusts, nodular structure in the outside | Sp +++; Py ++, Mc ++ |
| EHF, CIR | IR05-TVG13-4-1 | 23°52.684'S | 69°35.795'E | 3,292 | Basalts | Oxidized columnar chimney coated with red brown oxides, and fluid conduits | Cpy +++; Mc ++, Sp ++, Py ++ |
| EHF, CIR | IR05-TVG13-4-2 | 23°52.684'S | 69°35.795'E | 3,292 | Basalts | Oxidized columnar chimney coated with red brown oxides, and fluid conduits | Cpy +++; Mc ++, Sp ++, Py ++ |

| | | | | | | | |
|---------------------------------------|------------------|-------------|-------------|-------|------------------|---|------------------------------|
| EHF, CIR | IR05-TVG13-9.1 | 23°52.684'S | 69°35.795'E | 3,292 | Basalts | Irregular crust consisted of red brown to yellowish green oxide, anhydrite and gypsum, with disseminated sulfides | Py +++ |
| EHF, CIR | IR05-TVG13-9.2-1 | 23°52.684'S | 69°35.795'E | 3,292 | Basalts | Chimney fragment with red, brown and yellowish green mixture of oxide, anhydrite and gypsum | Mc +++; Cpy ++, Sp ++, Py ++ |
| EHF, CIR | IR05-TVG13-9.2-2 | 23°52.684'S | 69°35.795'E | 3,292 | Basalts | Chimney fragment with red, brown and yellowish green mixture of oxide, anhydrite and gypsum | Mc +++; Cpy ++, Sp ++, Py ++ |
| EHF, CIR | 19III-S18-TVG9 | 23°52.638'S | 69°35.850'E | 3,282 | Basalts | Porous Fe-Cu rich sulfides with minor sulfates | Py +++; Mc ++, Sp ++, Cpy ++ |
| <i>Slow-spreading mid-ocean ridge</i> | | | | | | | |
| LHF, MAR | MAR05-TVG1-9 | 14°45.186'N | 44°58.772'W | 3,025 | Ultramafic rocks | Porous Cu-rich massive sulfide | Cpy +++; Py ++ |
| LHF, MAR | MAR05-TVG1-10-2 | 14°45.186'N | 44°58.772'W | 3,025 | Ultramafic rocks | Fragment with gypsum, amorphous silica, disseminated marcasite and chalcopyrite | Cpy +++; Py ++ |
| LHF, MAR | MAR05-TVG1-10-3 | 14°45.186'N | 44°58.772'W | 3,025 | Ultramafic rocks | Fragment with gypsum, amorphous silica, disseminated marcasite and chalcopyrite | Cpy +++; Py ++ |
| LHF, MAR | MAR05-TVG1-21 | 14°45.186'N | 44°58.772'W | 3,025 | Ultramafic rocks | Cu-rich massive sulfides fragment with small cavities | Cpy +++; Sp +; Py + |
| 13°S, MAR | 21IV-S7-TVG4-1 | 13°17.203'S | 14°24.837'W | 2,311 | Basalts | Zn-Fe rich massive sulfide fragment coated | Sp +++; Py +++; Cpy + |

with Fe hydroxides and Cu sulfides

Ultra-slow spreading mid-ocean ridge

| | | | | | | | |
|--------------|-------------------|-------------|-------------|-------|---------|--|-----------------------------|
| area A, SWIR | 19II-S7-TVG4 | 37°47.004'S | 49°28.176'E | 2,781 | Basalts | Black porous massive sulfides | Sp +++, Py ++; Cpy + |
| area A, SWIR | 20V-S34-TVG16 | 37°46.812'S | 49°38.886'E | 2,780 | Basalts | Massive sulfide fragment with dark brown oxide crust | Py +++; Cpy + |
| area A, SWIR | 20V-S35-TVG17-1-1 | 37°46.812'S | 49°38.886'E | 2,783 | Basalts | Massive sulfide with dark brown oxide crust | Po ++, Py ++; Cpy + |
| area A, SWIR | 20V-S35-TVG17-3-2 | 37°46.812'S | 49°38.886'E | 2,783 | Basalts | Massive sulfide with dark brown oxide crust | Po ++, Py ++; Cpy + |
| area A, SWIR | 20V-S35-TVG17-4-1 | 37°46.812'S | 49°38.886'E | 2,783 | Basalts | Massive sulfide with dark brown oxide crust | Po ++, Py ++; Cpy + |
| area A, SWIR | 20V-S35-TVG17-7 | 37°46.812'S | 49°38.886'E | 2,783 | Basalts | Massive sulfide with dark brown oxide crust | Po ++, Py ++; Cpy + |
| area A, SWIR | 21VII-TVG22 | 37°56.316'S | 49°15.894'E | 1,443 | Basalts | Fe-rich chimney fragment coated with grey amorphous silica, conduits partially in-filled with oxides | Cpy +++, Py +++; Mc +, Sp + |

Back-arc basin

| | | | | | | | |
|------------|-----------|-------------|--------------|-------|---------|--|---------------------|
| S99HF, NFB | 26.1GTV-1 | 16°57.602'S | 173°54.991'E | 1,976 | Basalts | Inner Zn-rich chimney wall fragment with yellowish brown oxides | Sp +++; Mc +, Cpy + |
| S99HF, NFB | 26.1GTV-2 | 16°57.602'S | 173°54.991'E | 1,976 | Basalts | Inner Zn-rich chimney wall fragment with yellowish brown oxides | Sp +++; Mc +, Cpy + |
| S99HF, NFB | 26.2GTV-1 | 16°57.602'S | 173°54.991'E | 1,976 | Basalts | Greyish Zn-rich chimney fragment with local honeycomb structure and coarse black sphalerite crystals | Sp +++; Mc +, Cpy + |

| | | | | | | | |
|------------|------------|-------------|--------------|-------|---------|--|-----------------------|
| S99HF, NFB | 26.2GTV-2 | 16°57.602'S | 173°54.991'E | 1,976 | Basalts | Greyish Zn-rich chimney fragment with local honeycomb structure and coarse black sphalerite crystals | Sp +++; Mc +, Cpy + |
| S99HF, NFB | 26.2GTV-3 | 16°57.602'S | 173°54.991'E | 1,976 | Basalts | Greyish Zn-rich chimney fragment with local honeycomb structure and coarse black sphalerite crystals | Sp +++; Mc +, Cpy + |
| S99HF, NFB | 42GTV-2 | 16°57.533'S | 173°54.978'E | 1,975 | Basalts | Cu-rich chimney fragment with conduits | Cpy +++; Py ++, Mc ++ |
| S99HF, NFB | 42GTV-3 | 16°57.533'S | 173°54.978'E | 1,975 | Basalts | Cu-rich chimney fragment with conduits | Cpy +++; Py ++, Mc ++ |
| S99HF, NFB | 113.1GTV-1 | 16°57.322'S | 173°54.970'E | 1,967 | Basalts | Porous massive sulfide | Py ++, Cpy ++ |
| S99HF, NFB | 113.1GTV-2 | 16°57.322'S | 173°54.970'E | 1,967 | Basalts | Porous massive sulfide | Py ++, Cpy ++ |
| S99HF, NFB | 113.1GTV-3 | 16°57.322'S | 173°54.970'E | 1,967 | Basalts | Porous massive sulfide | Py ++, Cpy ++ |
| S99HF, NFB | 113.1GTV-4 | 16°57.322'S | 173°54.970'E | 1,967 | Basalts | Porous massive sulfide | Py ++, Cpy ++ |
| S99HF, NFB | 113.2GTV | 16°57.322'S | 173°54.970'E | 1,967 | Basalts | Porous massive sulfide | Py ++, Cpy ++ |

EPR—East Pacific Rise; KHF—Kairei Hydrothermal Field; EHF—Edmond Hydrothermal Field; CIR—Central Indian Ridge; SWIR—Southwest Indian Ridge; S99HF—Sonne 99

Hydrothermal Field; NFB—North Fiji Basin; LHF—Logatchev Hydrothermal Field; MAR—Mid-Atlantic Ridge. Py—pyrite; Mc—marcasite; Cpy—chalcopyrite; Sp—sphalerite;

Po—pyrrhotite. +++: abundant (>30%); ++: major (5-30%); +: minor (≤5%).

Table 2 Sulfur isotopic compositions of seafloor hydrothermal sulfide and sulfate minerals from the EPR near 1–2°S, 13°N and 11°N, KHF, CIR near 25°S, EHF, LHF, MAR near 13°S, area A, and S99HF.

| Sample No. | Mineralogy | $\delta^{34}\text{S}_{\text{VCDT}} (\text{‰})$ | Sample No. | Mineralogy | $\delta^{34}\text{S}_{\text{VCDT}} (\text{‰})$ |
|-------------------|------------|--|---------------------|------------|--|
| <i>1–2°S, EPR</i> | | | <i>EHF, CIR</i> | | |
| 20III-S4-TVG1-1-1 | Py | 5.82 | IR05-TVG12-11 | Py | 5.83 |
| 20III-S4-TVG1-1-2 | Py | 5.60 | IR05-TVG12-14 | Py | 6.57 |
| 20III-S4-TVG1-1-3 | Py | 5.47 | IR05-TVG13-4-1 | Cpy | 7.54 |
| 20III-S4-TVG1-1-4 | Py | 5.20 | IR05-TVG13-4-2 | Sph | 7.04 |
| 20III-S4-TVG1-2-1 | Py | 3.71 | IR05-TVG13-9.1 | Py | 6.03 |
| 20III-S4-TVG1-2-2 | Py | 3.52 | IR05-TVG13-9.1 | Sulfate | 21.5 |
| 20III-S4-TVG1-2-2 | Cpy | 3.82 | IR05-TVG13-9.2-1 | Sph | 6.61 |
| 20III-S4-TVG1-2-3 | Py | 3.57 | IR05-TVG13-9.2-2 | Py | 6.87 |
| 20III-S4-TVG1-2-3 | Cpy | 3.87 | 19III-S18-TVG9 | Py | 7.25 |
| 20III-S6-TVG3 | Py | 3.03 | 19III-S18-TVG9 | Cpy | 6.40 |
| 21III-S17-TVG13 | Py | 4.02 | <i>LHF, MAR</i> | | |
| <i>13°N, EPR</i> | | | MAR05-TVG1-9 | Cpy | 9.05 |
| EPR05-TVG1-2-1 | Py | 2.21 | MAR05-TVG1-10-3 | Cpy | 9.60 |
| EPR05-TVG1-2-4 | Py | 2.05 | MAR05-TVG1-21 | Cpy | 9.45 |
| EPR05-TVG1-3-2 | Py | 1.91 | <i>13°S, MAR</i> | | |
| EPR05-TVG1-3-3 | Py | 1.53 | 21IV-S7-TVG4-1 | Py | 4.45 |
| EPR05-TVG2-1-2 | Py | 1.43 | <i>area A, SWIR</i> | | |
| EPR05-TVG2-1-4 | Py | 1.47 | 19II-S7-TVG4 | Py | 5.66 |
| <i>11°N, EPR</i> | | | 20V-S34-TVG16 | Py | 6.98 |
| 1384-2-2 | Py | 2.19 | 20V-S35-TVG17-1-1 | Py | 4.20 |
| <i>KHF, CIR</i> | | | 20V-S35-TVG17-3-2 | Py | 5.00 |
| IR05-TVG-9-1 | Py | 1.82 | 20V-S35-TVG17-4-1 | Py | 4.40 |
| IR05-TVG-9-2 | Py | 2.16 | 21VII-TVG22 | Py | 0.00 |

| | | | | | |
|------------------|-----|------|-------------------|-----|------|
| IR05-TVG-9-3 | Py | 2.25 | <i>S99HF, NFB</i> | | |
| <i>25°S, CIR</i> | | | 26.1GTV-1 | Sph | 3.69 |
| 19III-S12-TVG6 | Cpy | 5.94 | 26.1GTV-2 | Sph | 4.07 |
| <i>EHF, CIR</i> | | | 26.2GTV-1 | Sph | 3.52 |
| IR05-TVG12-5-2 | Sph | 6.38 | 26.2GTV-1 | Py | 2.73 |
| IR05-TVG12-5-2 | Py | 5.22 | 26.2GTV-3 | Sph | 3.44 |
| IR05-TVG12-8-2 | Sph | 6.14 | 42GTV-3 | Py | 3.84 |
| IR05-TVG12-8-2 | Py | 6.25 | 113.1GTV-1 | Cpy | 4.21 |
| IR05-TVG12-8-4 | Py | 6.30 | 113.1GTV-2 | Py | 2.80 |
| IR05-TVG12-8-4 | Sph | 6.30 | 113.1GTV-4 | Py | 4.04 |
| IR05-TVG12-9-1 | Sph | 6.30 | 113.1GTV-4 | Cpy | 3.97 |
| IR05-TVG12-11 | Sph | 6.21 | 113.2GTV | Py | 3.28 |

Py–pyrite; Cpy–chalcopyrite; Sph–sphalerite.

Table 3 Comparison of sulfur isotopic compositions of seafloor hydrothermal sulfides from different deep-sea hydrothermal systems.

| Field | | | Field | | |
|---|--------------|------------|---|-------------|------------|
| $\delta^{34}\text{S}$ (‰) | | | $\delta^{34}\text{S}$ (‰) | | |
| Range | | | Range | | |
| Average (n) | | | Average (n) | | |
| <i>Super-fast spreading mid-ocean ridge</i> | | | <i>Super-slow spreading mid-ocean ridge</i> | | |
| 21°S, EPR | +4.5~+5.3 | +4.8 (4) | area A, SWIR | 0.0~+7.0 | +4.4 (6) |
| 16°43'S, EPR | +2.3~+6.3 | +3.7 (49) | <i>Sediment-hosted mid-ocean ridge</i> | | |
| 7°24'S, EPR | +1.4~+8.9 | +3.7 (31) | Middle Valley | -8.0~+12.4 | +6.0 (190) |
| 1–2°S, EPR | +3.0~+5.8 | +4.3 (11) | Escanaba Trough | -0.1~+11.6 | +5.0 (71) |
| <i>Fast-spreading mid-ocean ridge</i> | | | Guaymas Basin | -9.7~+11.1 | -0.2 (92) |
| 9–10°N, EPR | +0.7~+3.8 | +2.6 (36) | <i>Back-arc basin</i> | | |
| 11°N, EPR | +2.2~+4.9 | +4.1 (22) | Jade, Okinawa Trough | +3.2~+7.2 | +5.9 (14) |
| 13°N, EPR | +0.4~+5.0 | +2.7 (75) | Mariana Trough | +2.1~+3.1 | +2.7 (18) |
| 21°N, EPR | +0.7~+6.2 | +2.5 (118) | Manus Basin | -8.0~+6.0 | +1.2 (54) |
| <i>Intermediate-spreading mid-ocean ridge</i> | | | North Fiji Basin | +0.4~+5.6 | +3.5 (89) |
| Galapagos 86°W | +2.8~+5.5 | +3.9 (21) | Vai Lili, Lau Basin | +7.2~+16.2 | +9.4 (13) |
| SJdFR | +1.6~+5.7 | +3.2 (44) | White Church, Lau Basin | +2.2~+6.8 | +4.2 (20) |
| EHF, CIR | +5.2~+7.5 | +6.4 (17) | Hine Hina, Lau Basin | -7.2~+2.8 | -5.0 (12) |
| KHF, CIR | +1.8~+2.3 | +2.1 (3) | <i>Island-Arc volcano</i> | | |
| <i>Slow-spreading mid-ocean ridge</i> | | | Myojinsho Caldera | -5.3~+2.8 | +1.0 (6) |
| Lucky Strike, MAR | -0.9~+4.6 | +2.4 (65) | Conical Seamount | -17.5~+6.1 | -1.9 (129) |
| Rainbow, MAR | +0.5~+12.5 | +8.0 (64) | Brothers Seamount | -0.5~+2.9 | +1.6 (8) |
| Broken Spur, MAR | -0.8~+3.2 | +1.3 (48) | <i>Rift zone</i> | | |
| TAG, MAR | +0.35~+10.27 | +6.7 (287) | Red Sea | -16.2~+23.4 | +4.9 (74) |
| Snakepit, MAR | +1.2~+2.8 | +2.1 (16) | <i>Ridge-hotspot intersection</i> | | |
| LHF, MAR | +4.5~+9.6 | +5.7 (20) | Axial seamount, JdFR | +1.1~+9.4 | +4.2 (113) |

Data are from: 21°S, EPR (Ono et al., 2007); 16°43'S, EPR (Marchig et al., 1997); 7°24'S, EPR (Marchig et al., 1997); 1–2°S, EPR (this study, see Table 2); 9–10°N, EPR (Ono et al., 2007;

Rouxel et al., 2008); 11°N, EPR (Bluth and Ohmoto, 1988); 13°N, EPR (Bluth and Ohmoto, 1988; Ono et al., 2007; Stuart et al., 1995; Zeng et al., 2010; partly data from this study, see Table 2); 21°N, EPR (Arnold and Sheppard, 1981; Hekinian et al., 1980; Kerridge et al., 1983; Stuart et al., 1994a; Woodruff and Shanks, 1988; Zierenberg et al., 1984); Galapagos 86°W (Knott et al., 1995); SJdFR (Shanks and Seyfried, 1987); Edmond, CIR (this study, see Table 2); Kairei, CIR (this study, see Table 2); Lucky Strike, MAR (Ono et al., 2007; Rouxel et al., 2004a; Rouxel et al., 2004b); Rainbow, MAR (Lein et al., 2001; Rouxel et al., 2004b); Broken Spur, MAR (Bulter et al., 1998; Duckworth et al., 1995); TAG, MAR (Chiba et al., 1998; Gemmell and Sharpe, 1998; Herzig et al., 1998a; Knott et al., 1998; Lein et al., 1991; Stuart et al., 1994a; Zeng et al., 2000a); Snakepit, MAR (Kase et al., 1990; Stuart et al., 1994a); Logatchev, MAR (Rouxel et al., 2004b ; partly data from this study, see Table 2); A area, SWIR (this study, see Table 2); Middle Valley (Duckworth et al., 1994; Goodfellow and Franklin, 1993; Stuart et al., 1994a, b; Zierenberg, 1994); Escanaba Trough (Bühke and Shanks, 1994; Koski et al., 1988; Zierenberg et al., 1993; Zierenberg and Shanks, 1994); Guaymas Basin (Koski et al., 1985; Peter and Shanks, 1992; Shanks and Niemitz, 1982); Jade, Okinawa Trough (Halbach et al., 1989; Marumo and Hattori, 1999; Zeng et al., 2002a); Mariana Trough (Kusakabe et al., 1990); Manus Basin (Lein et al., 1993; Kim et al., 2004); North Fiji Basin (Kim et al., 2006; partly data from this study, see Table 2); Lau Basin (Herzig et al., 1998b); Myojinsho Caldera (Iizasa et al., 1992); Conical Seamount (Gemmell et al., 2004; Petersen et al., 2002); Brothers Seamount (de Ronde et al., 2003); Red Sea (Blum and Puchelt, 1991; Zierenberg and Shanks, 1988); Axial seamount, JdFR (Crown and Valley, 1992; Hannington and Scott, 1988). JdFR- Juan de Fuca Ridge; SJdFR-Southern Juan de Fuca Ridge. *n* - number of samples.

Table 4 Lead isotopic compositions of seafloor massive sulfide samples from EPR near 1–2°S and 13°N, KHF, CIR near 25°S, EHF, LHF, MAR near 13°S, area **A**, and S99HF.

| Sample No. | Mineralogy | ²⁰⁶ Pb/ ²⁰⁴ Pb | ²⁰⁷ Pb/ ²⁰⁴ Pb | ²⁰⁸ Pb/ ²⁰⁴ Pb | Pb (ppm) |
|-----------------------------|--------------------|--------------------------------------|--------------------------------------|--------------------------------------|----------|
| <i>1–2°S, EPR</i> | | | | | |
| 20III-S4-TVG1-1-2 | Py | 18.185±0.001 | 15.488±0.001 | 37.760±0.002 | 78.8 |
| 20III-S4-TVG1-2-3 | Cpy+Py±Sph | 18.156±0.001 | 15.451±0.001 | 37.635±0.003 | 77.9 |
| 20III-S6-TVG3 | Py+Sph | 18.259±0.002 | 15.512±0.002 | 37.877±0.005 | 560 |
| <i>13°N, EPR</i> | | | | | |
| EPR05-TVG1-2-2 | Py | 18.431±0.001 | 15.518±0.001 | 37.974±0.002 | 59.3 |
| EPR05-TVG1-3-1 | Py | 18.457±0.001 | 15.553±0.001 | 38.080±0.002 | 99.7 |
| EPR05-TVG2-1-1 | Py+Sph±Cpy | 18.419±0.001 | 15.506±0.001 | 37.920±0.004 | 256 |
| <i>KHF, CIR</i> | | | | | |
| IR05-TVG-9-2 | Py | 18.471±0.002 | 15.597±0.002 | 38.406±0.007 | 37.3 |
| <i>25°S, CIR</i> | | | | | |
| 19III-S12-TVG6 | Cpy±CuS±oxide | 17.553±0.004 | 15.503±0.004 | 37.600±0.010 | 1.54 |
| 19III-S12-TVG6 ^a | Cpy±CuS±oxide | 17.541±0.004 | 15.491±0.003 | 37.557±0.008 | |
| <i>EHF, CIR</i> | | | | | |
| IR05-TVG12-14 | Py | 17.898±0.001 | 15.453±0.001 | 37.815±0.002 | 1905 |
| IR05-TVG13-4-2 | Cpy+Py | 17.957±0.001 | 15.515±0.001 | 38.023±0.005 | 1374 |
| IR05-TVG13-9.2-1 | Py+Sph+Cpy | 17.984±0.002 | 15.562±0.002 | 38.173±0.007 | 1312 |
| 19III-S18-TVG9 | Py±sulfate | 17.921±0.001 | 15.483±0.001 | 37.910±0.003 | 442 |
| <i>LHF, MAR</i> | | | | | |
| MAR05-TVG1-9 | Cpy+CuS+Py±sulfate | | | | 19.1 |
| | (<1%) | 18.698±0.001 | 15.684±0.001 | 38.988±0.002 | |
| MAR05-TVG1-10-2 | Py+Cpy±sulfate | | | | 15.4 |
| | (2%) | 19.268±0.001 | 15.583±0.001 | 38.959±0.002 | |
| <i>13°S, MAR</i> | | | | | |

| | | | | | |
|---------------------|--------|--------------|--------------|--------------|-------|
| 21IV-S7-TVG4-1 | Py | 18.310±0.002 | 15.534±0.002 | 38.172±0.007 | 850 |
| <i>area A, SWIR</i> | | | | | |
| 20V-S35-TVG17-7 | Py | 18.208±0.001 | 15.491±0.001 | 37.997±0.002 | - |
| 21VII-TVG22 | Py | 18.149±0.002 | 15.484±0.002 | 37.988±0.005 | 17.4 |
| <i>S99HF, NFB</i> | | | | | |
| 26.2GTV-2 | Py+Sph | 18.146±0.001 | 15.514±0.001 | 38.001±0.003 | 1198 |
| 42GTV-2 | Py+Cpy | 18.160±0.001 | 15.493±0.001 | 37.969±0.003 | 965 |
| 113.1GTV-3 | Py+Cpy | 18.146±0.001 | 15.505±0.001 | 37.983±0.002 | 781.6 |
| 113.2GTV | Py | 18.139±0.001 | 15.499±0.001 | 37.960±0.002 | 1343 |

All Pb isotopic ratios measured by static mode were corrected for instrumental mass fractionation through repeated analyses of the NBS 981 standard. Analytical error (2σ) is reported for each ratio. The Pb contents of the hydrothermal sulfide samples were determined on separate 40 mg splits of bulk sulfide by ICP-AES, relative standard deviation (RSD) <2%. ^a Indicates the repeated analysis sample; “-” Indicates no data available.

| | | | | | | |
|------------------------------------|---------------|-------------|---------------|-------------|---------------|-------------|
| Jade, Okinawa Trough | 18.491-18.609 | 18.544 (13) | 15.580-15.684 | 15.622 (13) | 38.570-38.859 | 38.696 (13) |
| Eastern Manus Basin | 18.760-18.780 | 18.775 (6) | 15.520-15.540 | 15.530 (6) | 38.310-38.400 | 38.357 (6) |
| North Fiji Basin | 18.082-18.193 | 18.138 (19) | 15.440-15.554 | 15.492 (19) | 37.764-38.150 | 37.949 (19) |
| Lau Basin | 18.615-18.690 | 18.667 (4) | 15.531-15.550 | 15.540 (4) | 38.287-38.327 | 38.310 (4) |
| <i>Off-axis volcanoes</i> | | | | | | |
| Pito Seamount | 18.448-18.520 | 18.493 (6) | 15.482-15.583 | 15.548 (6) | 37.784-38.208 | 38.035 (6) |
| <i>Ridge-hotspot intersections</i> | | | | | | |
| Axial seamount, JdFR | 18.598-18.613 | 18.608 (3) | 15.457-15.458 | 15.457 (3) | 37.994-38.109 | 38.041 (3) |

Data are from: area A, SWIR (this study, see Table 4); TAG, MAR (Andrieu et al., 1998; Zeng et al., 2000b); LHF, MAR (this study, see Table 4); 25°S, CIR (this study, see Table 4); EHF, CIR (this study, see Table 4); Galapagos 86°W (Fouquet and Marcoux, 1995; LeHuray et al., 1988); Explorer Ridge (Fouquet and Marcoux, 1995); Endeavour Segment (LeHuray et al., 1988; Yao et al., 2009); SJdFR (LeHuray et al., 1988; Hegner and Tatsumoto, 1989); 21°N, EPR (Brévert et al., 1981; Vidal and Clauer, 1981); 13°N, EPR (Fouquet and Marcoux, 1995; Zeng et al., 2010; this study, see Table 4); 1–2°S, EPR (this study, see Table 4); 17°26'S, EPR (Fouquet and Marcoux, 1995); 18°31'S, EPR (Fouquet and Marcoux, 1995); 21°26'S, EPR (Fouquet and Marcoux, 1995); Middle Valley (Bjerkgård et al., 2000; Stuart et al., 1999; Cousens et al., 2002; Goodfellow and Franklin, 1993; Fouquet and Marcoux, 1995); Escanaba Trough (Zierenberg et al., 1993; LeHuray et al., 1988); Guaymas Basin (LeHuray et al., 1988); Jade, Okinawa Trough (Halbach et al., 1997; Zeng et al., 2000a); Eastern Manus Basin (Kim et al., 2004); North Fiji Basin (Kim et al., 2006; this study, see Table 4); Lau Basin (Fouquet and Marcoux, 1995); Pito Seamount (Verati et al., 1999); Axial seamount, JdFR (LeHuray et al., 1988). JdFR- Juan de Fuca Ridge; SJdFR-Southern Juan de Fuca Ridge. *n* - number of samples.

Highlights

- New S and Pb isotope analyses were performed on sulfides from MORs and BAB
- Basalt contributed comparable amounts of sulfur and lead to sulfides in MORs
- Discrete degree or variation rate can be used to study S and Pb isotopic **variations**
- **S and Pb sources and fluid processes** jointly affect S and Pb isotopic **compositions**